6.0 ANALYST TRAINING AND CERTIFICATION

6.0 ANALYST TRAINING AND CERTIFICATION

6.1 RATIONAL

Consistent with requirements by the EPA and other regulatory agencies for analyst training and certification programs, WWES has a strict policy relative to the training and certification of analysts prior to their involvement in the analysis of client samples. The program is necessary in order to maintain continuity in all analytical programs and to insure the integrity of all data.

6.2 TRAINING

The supervisor is responsible for training all new personnel. This training will be in conjunction with the group (workstation) and group leader if applicable. Training will include, but not be limited to, WWES QC requirements, paperwork flow, lab safety and organizational structure. In addition, the new analyst will be given copies of the QC manual, log-in manual and methodologies which the analyst will be required to read. Training in the methods to be used will be initiated prior to analyst certification.

6.3 CERTIFICATION

Each new WWES analyst will be required to receive certification on all methods which he is to perform. Certification insures that the analyst can meet WWES detection limits and quality control limits as established for the method. Certification includes two parts, both of which must be completed satisfactorily.

6.3.1 Method Spikes

Analysis of spiked lab pure water at the levels of 0.5x, 1.0x, 2.0x, 5.0x and 10x where x is the established detection limit. This will include 2 blanks and a duplicated spike at 2.0x or 5.0x and will occur on 2 separate days. The data, where the duplicated results are averaged. These results must match current WWES Schwart control chart limits. Additional parameters such as consistent instrument calibration curves will be evaluated.

6.3.2 Check Sample Analysis

The analyst will test a known blind check sample in duplicate including a blank. All the data must fall within established control limits for the parameters.

6.3.3 Current Analysts Training

The LDI analyst, who is assigned a new method, must complete the certification program for the methods as outlined above prior to performing analyses on client samples.

6.4 RECERTIFICATION

All WWES analysts will recertify on all their respective methods when required or demonstrated by two method spike performance failures following the procedures set forth in Section 6.3.1. The results must meet previous data, assuming that the same methods are employed.

6.5 PERFORMANCE AUDITS

The Laboratory Manager, in cooperation with the QA Manager, will perform individual audits on all aspects of the operation biannually. These audits will include recertification data, control limits, all levels of records and laboratory performance on all check samples and instituted blind QC samples. A report of the audit results including recommendations will be forwarded to the President of the Environmental Laboratory Division.

7.0 DOCUMENT CONTROL, FLOW AND STORAGE

7.0 DOCUMENT CONTROL, FLOW AND STORAGE

7.1 PURPOSE

The paperwork trail must be designed to insure that after the issuance of a report, anyone - a client, a lawyer or the President of WWES can track a single sample result back through WWES records to the origin of the standards used in calibration and the identity of the person who prepared the sample bottles.

7.2 PAPERWORK FLOW

As shown in the attached, "Flow Diagram" the paperwork trail is eventually the same for routine work as it is for samples under Chain-of-Custody. The general axiom is that a COC procedure is doomed to failure without a pre-existing scheme of tight sample and analytical control available as a routine measure. This contention, however, is only of minimal consequence with respect to the need for detailed records. The records trail can provide the following:

- Answers to questions of analytical integrity for results which are 2 months or two years old.
- Assistance in finding and solving random and systematic problems.
- Assistance in preventing long term degradation of analytical integrity.
- Assistance in insuring continuity of analytical effort despite personnel and mechanical changes.

7.3 DOCUMENT REQUIREMENTS

The following subsection identifies all documents which are generated during the course of any project:

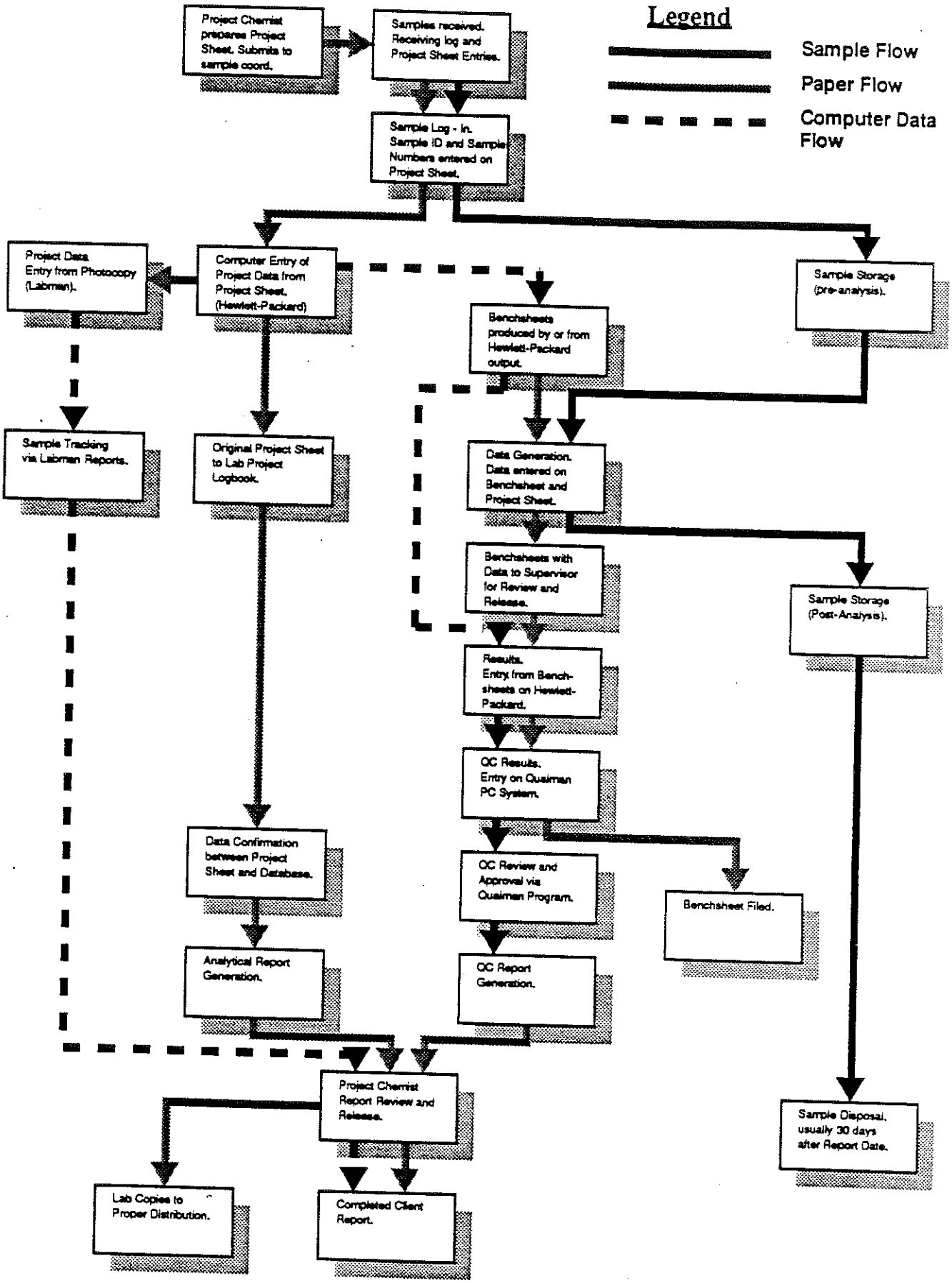
7.3.1 Project Sheets

Every sample or group of samples which enter the WWES facility must be accompanied by the appropriate project sheet which has been properly filled out and provided to the Sample Coordinator (SC). The SC may not log-in samples for which there are not project sheets or for which there the project sheet is incomplete. An example project sheet is attached as Figure 2.

7.3.2 New Project Approval Form

Projects which require testing or analyses not routinely provided at WWES must have prior approval on a Project Questionnaire and commitment from the Analytical Manager and the head of the appropriate analytical group(s). For the project manager's purpose, the approval forms insure that the analytical testing

Sample and Document Flow Diagram



ENVIRONMENTAL LABORATORY DIVISION
Project Initiation

Client Name _____
(32 characters available)

Report Address _____

_____

_____

_____, _____ _____ - _____

Billing Address
(if different) _____

_____

_____

_____, _____ _____ - _____

Client Alias _____

Client Contact _____
(20 characters available)

Phone (_____) _____ - _____ Ext. _____

Project Chemist _____

Client Expiration Date _____ - _____ - _____ Narrative _____

Space for the Client Narrative is provided on the back side of this sheet

Project Description _____

_____
(2 lines of 26 characters available)

Price Code _____ Price Factor _____

Price Code Expire Date _____

Project Contact _____

Phone (_____) _____ - _____ Ext. _____

Project Expiration Date _____

Purchase Order No. _____ Proj. Type[1] _____ Report Format[2] _____

Contract No. _____ Field Blanks _____ Methods Page _____

CCS Mgr. _____ Case Narr. _____ QC Report _____

CCS Project No. _____

[1] C = Competitive Quote; D = Direct Request; R = Renewal

Frequency (1) ___ Turnaround ___ Flame ___ Bottles (4) ___

Submit/Yr. ___ C.O.C. (2) ___ Reactive ___ Carrier ___

# of Samples ___ QC Type (3) ___ Contact ___ Sample Storage ___

Health ___ Bottle Address (5) ___

Narrative ___

(1) Days between submittals
(2) I = Internal (Lab)COC; E = External (Field)COC; N = None
(3) RAS, SAS, QAP
(4) H = Hold; S = Ship
(5) Y = Yes if Bottle Address is Different than Client Address

Bottle Shipping Address

_____

_____

_____

_____

Space for the Project Narratives is provided on the back side of this sheet

Submittal Description ___
(26 characters available)

Date Expected ___ - ___ - ___

Bottle Due Date ___ - ___ - ___

Turnaround Days ___

Narrative ___

Submittal Narrative

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

Figure 2

Test Group Description
(40 characters available)

Sample Matrix

Date Expected - -   Bottle Due Date - -

Parameters	Method Number (Reference Citation)	Specific DL

Figure 2

area has received notification and will be prepared. For the analytical managers purpose, proper notification has been received and sufficient time has been allotted for preparation and development. Projects requiring rush turn around on modified methods must be approved as well. An example of a Project Questionnaire is attached as Figure 3.

7.3.3 Problem Project Sheets

When the Sample Coordinator (SC) identifies a problem with a sample shipment or project sheet, a Problem Project Sheet will be initialed and sent to the project manager for resolution. See Figure 4.

7.3.4 Chain-of-Custody Forms

There are three forms for Chain-of-Custody samples. All three forms must be properly completed and included in the project file for each and every COC project.

7.3.4.1 COC Shipping Record

The shipping record must be received in the shipping container with every COC shipment. The form attached as Figure 5 is similar to the form used by the EPA. This form will be used by WWES field samplers and returned with the samples. Other forms of a similar nature may be used by other clients. However, the information required on the WWES form must be present on any other client form or they run the risk of their COC being rejected as a continuous trackable COC event.

7.3.4.2 COC Sample Control Record

This form is used as a record of the movement of COC samples in and out of the COC locked storage. The analyst signs samples in and out each time a sample(s) is removed for any analysis. A copy of the form is attached as Figure 6. After all analyses are complete, the Sample Coordinator files the form in the COC project file.

7.3.5 Work Sheets/Project Sheets

Work sheets are the analytical assignment forms generated by the computer or the lab manager within 24 hours after log-in for each project or group of projects. The work sheets are divided into work stations, i.e. the analytes for which one or more analysts has sole responsibility.. In many cases, the work sheets will have an entry position for the results of each analyses for each sample. In either case, the work sheet, upon completion of all analyses, will be turned into the appropriate

ENVIRONMENTAL LABORATORY DIVISION
PROJECT QUESTIONNAIRE

REQUEST FOR WORK/QUOTATION
(circle one)

1a. Client _____ Proj. No. _____

1b. Project Name_____Proj. Mgr._____ Initials: __
(How do you want it to look on the report)?

2. Where should report be routed?_____

3. Date of request of work?_____Lab Notified YES NO_____

4. Date samples will arrive in lab:_____

5. Project Frequency: One Time _____ Other (specify) _____

6. Turnaround required _____ Due Date:_____Time:_____
Confirmed in ELD by: _____

7. Job Description:_____

8. Quality control requirements: RAS SAS QAP

9. Does QC need to be reported? YES NO

10. Is strict Laboratory Chain of Custody required? YES NO

11. Have sample containers been requested? YES NO

12. Sample containers for the project have requested from Grand Rapids/Livonia (circle one).

13. **No. of water samples:**_____

14. Parameters required are or/see attached (circle one):_____
_____
_____
_____
_____
_____

15. Specific methods, detection limits, and/or program requirements (e.g. NPDES, Act 307 . . .)
_____
_____
_____
_____
_____

16. **No. of soil samples:**_____

17. Parameters required are or/see attached (circle one):_____
_____
_____
_____
_____
_____

18. Specific methods, detection limits, and/or program requirements (e.g. RCRA, Act 307, etc.)
_____
_____
_____
_____
_____

19. **No. of air samples:**_____

20. Parameters req ired are or/see attached (circle one):_____

21. Specific methods, detection limits, and/or program requirements (e.g. ACGIH, TLV, etc.)

22. **No. of other samples:** _____ Type:_____

23. Parameters required are or/see attached (circle one):_____

24. Specific methods, detection limits, and/or program requirements (e.g. Act 307, RCRA, etc.)

25. Hazard levels associated with the samples are:_____

26. Has the client has been advised that any hazardous samples will be returned to them? YES NO

27. Disposal of samples will take place 21 to 30 days after report mailing unless noted otherwise. _____ (If otherwise is noted a charge of $5/sample month will apply).

28. Costs for the analysis were confirmed by (ELD) _____ of the Grand Rapids Branch.

29. Is there any particular format needed for the final report? YES NO (If yes discuss with ELD Project Chemist)

30. Are there any field measurements to be reported? YES NO
If so specify _____

31a. Are you running field blanks? YES NO

31b. Are you running trip blanks? YES NO

32. Other Information:

33. Lab signature_____

34. CCS signature_____

FIGURE 4

WWES LABORATORY
PROBLEM PROJECT REPORT

SAMPLES RECEIVED ON _____ AT _____ AM/PM FROM: _____

AND DESCRIBED AS _____ WERE RECEIVED HAVING THE FOLLOWING DEFICIENCIES.

____ WWES PROJECT APPROVAL FORM - ABSENT/INCOMPLETE

____ CHAIN-OF-CUSTODY - ABSENT/INCOMPLETE

____ CHAIN-OF-CUSTODY - DOES NOT MATCH SAMPLE TAGS

____ SAMPLE BOTTLES - BROKEN

____ SAMPLES ABSENT - QUAN. DOES NOT MATCH APPROVAL FORM

____ SAMPLE BOTTLES - INCORRECT FOR ANALYSIS

____ SAMPLE PRESERVATIVES - INCORRECT FOR ANALYSIS

____ SAMPLE VOLUMES - INCORRECT FOR ANALYSIS

____ SAMPLE TAGS - WRONG I.D./ABSENT

____ FIELD FORMS - ABSENT/INCOMPLETE

____ CUSTODY SEALS - ABSENT/NOT INTACT

____ NON-ROUTINE PROJECT - NO PRIOR APPROVAL

THE SAMPLES IN QUESTION WILL BE PROCESSED AS IS ____ PLACED ON HOLD ___
UNTIL THE CORRECTIVE ACTIONS OR DIRECTIVES ARE ISSUED.

THANK YOU
WWES LABORATORY
SAMPLE COORDINATOR

Kriscunas3/ppr

WW Engineering & Science, Inc.
Environmental Laboratory Division
6665 Glenwood Hills Pkwy SE • PO Box 874
Grand Rapids, Michigan 49588-0874

Chain of Custody Record

№ 27823

Project No.	Project Name							
Samplers (signature)								
Date	Time	Matrix*	Comp	GRAB	Sample I.D.	No. of Containers	Container Type & Volume	Preservation Method	Analysis Required/Comments

Relinquished by: (signature)	Date / Time	Received by:	Relinquished by:	Date / Time	Received by: (signature)	
Dispatched by: (signature)	Date / Time	Carrier:	Received to lab by:	Date / Time	Logged in by:	Date/Time

* MATRIX: WATER (WTR), WASTEWATER (WW), SOIL (SOL), SLUDGE (SLU), AIR, OIL, HAZARDOUS WASTE (HW)

03 EDI/Chain of Cust-Disk Files

CHAIN OF CUSTODY

CLIENT: Rumpke of Ohio, Inc.

PROJECT: Quarterly Monitoring
Cincinnati, Ohio Landfill

SUBMITTAL: August, 1991 Groundwaters
PARAMETER: CARBON, TOTAL ORGANIC

METHOD: TOC/OXID/WTR

SAMPLE #	REMOVED BY: (SIGNATURE)	DATE & TIME REMOVED	RELINQUISHED BY: DATE & TIME	RECEIVED BY: DATE & TIME	DATE & TIME RETURNED
1279					
1280					
1281					
1282					
1283					
1284					
1285					

Figure 6

supervisor with the proper bench sheets attached. Unless specifically advised, data will not be accepted on any form other than the project approval form sheets.

7.3.6 Bench Sheets

The analysis of every analyte or group of analytes needed, i.e. VOA's requires a specific bench sheet which includes all results from the analysis of a group of samples. There are specific bench sheets for each analyte including specific requirements for their use. Examples of each bench sheet, can be found in Figures 7, 8 and 9.

7.3.7 Lab Notebooks

The lab notebooks are the daily records of all activities of an analyst, or group of analysts, working in the lab. The notebooks will be bound and paginated. The notebook will be cleanly labeled on the inside cover with the date issued, the analyst's name, and the date completed. There are several specific rules which will be follows:

- All entries are in ink
- There are no erasures, obliterations, or white outs allowed
- Corrections are single lined and initialed
- A new page is started each day or with every batch of samples
- Empty space is covered with a Z and signed and dated across the obtuse line
- Any and all work, observations and errors are noted
- Problem areas identified

When the instrument has just been repaired, a lamp changed, new column installed, detector repaired, or changed in any other manner, the log will also contain:

- A comment relative to the change or repair
- Reference page number to the Instrument Maintenance Log

The organic log books will also contain the following information relative to GC and GCMS oven and column conditions UNLESS they are exactly as specified in the referenced method which then will be commented on as such:

- column used (packing, diameter, length, type) o capillary as split or splitless
- current type and flow
- make up flow if appropriate
- oven temperature and program if appropriate
- injector temperature
- detector temperature
- ion chamber voltage (GCMS)

05-SEP-91

METALS BENCHSHEET

Test #: 198.01- 71.01
Parameter: COPPER, TOTAL
Method: FLAME/CU/WTR ODL: 0.01
Ref. Cit.: USEPA-220.1 Unit: mg/l

Instrument #:
Benchsheet ID: 2482
Owner:
Date run:
Reviewed By:
Est anal hrs: 1.6
Act anal hrs:
Samples in batch: 8
Stock std #:

Comments:

Client Submittal	Sample	COC	QC	Reported Conc.	Duplicate Result	Spike Result	Spike Qty.	Spike Stock #	% dif	% rec	ODL	Analyst	EXC	DNR
ICB:							XXXXXXXX	XXXXXXXX						
							XXXXXXXX	XXXXXXXX						
ICV: Stk														
GM BOC Lansing 453- 1	1720		RAS											
GM BOC Lansing 453- 1	1721		RAS											
GM BOC Lansing 453- 1	1722		RAS											
GM BOC Lansing 453- 1	1723		RAS											
GM BOC Lansing 453- 1	1724		RAS											
GM BOC Lansing 453- 1	1726		RAS											
GM BOC Lansing 453- 1	1727		RAS											
GM BOC Lansing 453- 1	1728		RAS											
MPB:							XXXXXXXX	XXXXXXXX						
							XXXXXXXX	XXXXXXXX						
Digested LCS: Stk														
LCS: Stk							XXXXXXXX	XXXXXXXX						
CCB:							XXXXXXXX	XXXXXXXX						
CCV: Stk														

UUES/ENVIRONMENTAL LABORATORY DIVISION

Figure 7

Test #: 376.01- 35.01
Parameter: VOLATILE'S GC/MS 8240
Method: VOL/P&T/MS/WTR
Ref. cit.: USEPA-8240 Unit: ug/l

Client: 3M Company/St. Paul, Minnesota
Project: 428 3M Request # J2496
Main Plant
Submittal: 1 Volatile Organics Analysis
Sample: 1422 J2496-1

Expiration date: 05-SEP-1991 QC: RAS COC:
Lab due date: 05-SEP-1991
Client due date: 12-SEP-1991 C=0 F=0 H=1 R=0

Benchsheet ID: 2466
Owner: _____
Date run: _____
Instrument #: _____
Est anal hrs: 1
Act hrs: _____
Stock std #: _____
Supervisor: _____

*** SEMI-VOLATILES ORGANICS ***
Initial wt./vol. _____
Final volume _____
Dilution factor _____

***** VOLATILES ORGANICS ******
Initial wt./vol. _____
Volume purged _____
Dilution factor _____

	Parameter	Result
1.	ACETONE	< 50
2.	BENZENE	< 1.0
3.	BROMODICHLOROMETHANE	< 2.0
4.	BROMOFORM	< 15
5.	BROMOMETHANE	< 10
6.	2-BUTANONE	< 50
7.	CARBON DISULFIDE	< 5.0
8.	CARBON TETRACHLORIDE	< 4.0
9.	CHLOROBENZENE	< 1.0
10.	CHLOROETHANE	< 10
11.	2-CHLOROETHYLVINYL ETHER	< 10
12.	CHLOROFORM	< 1.0
13.	CHLOROMETHANE	< 10
14.	DIBROMOCHLOROMETHANE	< 3.0
15.	1,1-DICHLOROETHANE	< 2.0
16.	1,2-DICHLOROETHANE	< 2.0
17.	1,1-DICHLOROETHYLENE	< 2.0
18.	1,2-DICHLOROETHENE(TOTAL)	< 4.0
19.	1,2-DICHLOROPROPANE	< 3.0
20.	CIS-1,3-DICHLOROPROPENE	< 4.0
21.	TRANS-1,3-DICHLOROPROPENE	< 4.0
22.	ETHYL BENZENE	< 1.0
23.	2-HEXANONE	< 50
24.	4-METHYL-2-PENTANONE	< 50
25.	METHYLENE CHLORIDE	< 5.0
26.	STYRENE	< 10
27.	1,1,2,2-TETRACHLOROETHANE	< 2.0
28.	TETRACHLOROETHENE	< 2.0
29.	1,1,1-TRICHLOROETHANE	< 2.0
30.	1,1,2-TRICHLOROETHANE	< 3.0
31.	TRICHLOROETHENE	< 2.0
32.	TOLUENE	< 1.0
33.	VINYL ACETATE	< 5.0
34.	VINYL CHLORIDE	< 10
35.	XYLENE(S)	< 5.0

Parameter	Result

05-SEP-91 INORGANIC BENCHSHEET -- AUTOMATED CHEMISTRY PAGE 1

Test#: 389.01- 245.01
Parameter: CHLORIDE
Method: CL/TRAACS/WTR ODL: 2.0
Ref. Cit.: USEPA-325.2 Unit: mg/l

	STD VAL	OBS VAL	WKG STD NUMBER
1.			
2.			
3.			
4.			
5.			

Instrument #:
Benchsheet ID: 2463
Owner:
Date run:
Supervisor:
Est anal hrs: 8
Act anal hrs:
Samples in batch: 8
Stock std #:
Wavelength (nm):
Cell path (mm):

Comments:

Client..... Submittal	Sample	COC	QC	Wt/dil factor	Reported Conc.	ODL	Spike Qty	% rec/dif	EXC	DNR
ICB:							XXXXXXXX			
							XXXXXXXX			
ICV: Stk										
Rumpke of Indiana, Inc.										
231- 7	1701	YES	RAS							
Rumpke of Indiana, Inc.										
231- 7	1702	YES	RAS							
Rumpke of Indiana, Inc.										
231- 7	1703	YES	RAS							
Nor-Am Chemical Co.										
411- 1	1368		RAS							
Nor-Am Chemical Co.										
411- 1	1369		RAS							
Nor-Am Chemical Co.										
411- 1	1370		RAS							
Nor-Am Chemical Co.										
411- 1	1371		RAS							
Nor-Am Chemical Co.										
411- 1	1372 *		RAS							
MPB:							XXXXXXXX			
							XXXXXXXX			
LCS: Stk										
SPK: Stk	Smp									
DUP:	Smp						XXXXXXXX			
							XXXXXXXX			
CCB:							XXXXXXXX			
							XXXXXXXX			
CCV: Stk										

UWES/ENVIRONMENTAL LABORATORY DIVISION

Figure 9

7.3.9 Instrument Maintenance Log

The instrument maintenance log is a bound and paginated log which is used to track potential maintenance problems. The log is used every time the instrument is used but may contain several entries on one page. Entries on days where calibrations are correct may be as simple as "calibration met requirements". Anytime the instrument is repaired or modified in any way, the event must be noted with all specifics, including what was done, by whom, and why. A two detector GC has one log tracking, two detectors.

7.3.10 Oven, Refrigerator and Freezer Temperature Logs

Each oven, insulator or furnace, plus all cold storage devices, will have their temperatures checked and recorded daily, or at a minimum, 5 days a week. Each device will have a thermometer in place or a temperature recorder in-place which will be checked by the Data Coordinator. A bound log book with 31 entries will be used to record all entries for each device upon which the DC will record the date and temperature and will initial the entry. The DC will have an NBS thermometer which will move between devices to act as a QC check for the primary temperature device. The log will include the second temperature when measured monthly.

7.3.11 Balance Logs

An Area Analyst will check all balances in the laboratory every day (or at least 5 days a week) using NBS class S weights. The analyst will record each day's reading in a log developed to handle every balance. A balance which fails to meet criteria will be removed from service until repaired. The DC will insure that every balance is serviced and calibrated annually recording such service in the log.

7.3.12 Standard Record Books

Every standard used in the laboratory must be labeled and the label will possess the following information:

- The analyte or analytes contained in the standard
- The concentration
- The solvent
- The preservative, i.e. nitric acid
- The date made
- The Standard Reference Number

The last item, Standard Reference Number, is the identified standard and dilution sequence no. taken from the Standard Record Book in which the standard solution data is recorded.

All standards (including dilutions) will be recorded in a Standard Record Book assigned to the work station. Two record books will be used, each of which has a different purpose. The record books are subtitled as follows:

7.3.12.1 STOCK STANDARDS LOG

This book contains standards starting with the identification of the starting material. One standard and/or standard mix with it's corresponding dilutions are identified.

7.3.12.2 WORKING STANDARDS LOG

A working standard reference number is assigned and the corresponding dilutions are identified.

7.3.13 Control Charts

Each analytical method will require at least one control chart. Some tests may involve several control charts, i.e. duplicate, matrix spikes and method spikes. The QC coordinator will supply the limits to be used to the work station involved. Every data point generated with every analytical batch will be plotted on the chart. Every out-of-control data point will be noted and an action indicated as to the disposition of the data. Completed control charts will be turned in to the DC for permanent change.

7.3.14 Preliminary Reports

After all data has been entered for a project, the computer will flag a project ready for a preliminary report. The report will be identical to the final report in content except for the following:

- Preliminary Report will be reviewed and corrected if necessary on each page in large type.
- Comments necessary to the project will be printed under each sample or at the end of the report.

The DC will print the preliminary report and issue a copy along with the project file to the lab supervisor for review and corrections. The supervisor will sign off on the preliminary report after including comments, if appropriate, indicating that corrections are necessary. Afterwards, the supervisor(s) will pass the preliminary report to the QC Supervisor (QC) who will review and correct the report including a signature and comment. The QC will return the preliminary report

and file to the DC. The DC will make all corrections as required and review report structure for completeness. If no corrections are required, the DC will sign and date the preliminary report and place it in the Project File. The DC will then print a Final Report. When corrections are necessary, the DC will execute all corrections and indicate such changes on the initial preliminary, which is then filed in the project file. A new preliminary is then printed and issued for review.

7.3.15 Final Report

After the preliminary report has been corrected and cleared all reviews, the DC will manually alter the computer flag and print a Final Report which will be placed in the project file folder and forwarded to the AM for approval. Space will be provided on the c.o.c. project file folder for the signatures of the Analytical Manager, the QA Manager and the Project Manager, all of whom are thus certifying that the report is complete, correct and defensible. The DC will then arrange for delivery of the final report.

7.3.16 Project Files

The Project File is the comprehensive record of every project completed at WWES. A project file initially consists of a file folder set up by the Lab Secretary (LC) at the time of log-in. Chain-of-Custody projects will be stored in a locked COC file with strict limited access while routine project files are stored in a separate nominally limited access file. The LS will be responsible for including the following in the project file:

- Project Sheets
- Project Approval Sheets (if applicable)
- Problem Project Sheets
- Chain-of-Custody Forms
- All correspondence or documents received with the samples
- Preliminary Reports
- Separate Report Papers, i.e. Field Reports (if applicable) - Final Report
- Any additional paperwork which may follow the report

All project files are stored for a period of 4 years.

8.0 SAMPLE CONTROL, FLOW, AND STORAGE

8.0 SAMPLE CONTROL, FLOW, AND STORAGE

All samples received at the WWES Engineering and Sciences must be logged in before any work is performed on the samples. This procedural requirement is specific not only to the chemistry lab, but the microbiological laboratory. The purpose of the log-in procedure, including sequential numbers assigned to all samples received in the facility, is to insure that WWES has a means by which samples can be tracked, data can be stored, and quality control can be tracked for any sequence of events during a particular analytical period. In handling projects in this manner, WWES, or the client, can insure a consistent and documented sequence of events under any analytical situation.

Management acknowledges that there are situations in which log-in of samples will be difficult due to rapid turn around requirements for particular compounds that may decompose or volatilize. An example of this kind of analysis is the total coliform samples which can be anticipated and for which holding times are short. The project approval form discussed within this manual will make it possible to preassign project numbers to samples arriving at the facility. Should a secondary mode of operation be necessary for the receipt of such samples, a mechanism will be developed between the sample coordinator and the Quality Assurance Supervisor. Any deviation from the standard log-in procedures detailed herein will be at the discretion of the laboratory supervisor or the laboratory manager. The execution of the log-in procedures for Chain-of-custody samples (see Section 8.8) is extremely crucial. Samples, that have been designated for Chain-of-Custody by a client, possess the potential of involvement in litigation or other legal situations., i.e. standards development or patents. By breaking Chain-of-Custody requirements, all results are invalid for such purposes.

8.1 PROJECT INFORMATION

All information relative to a specific project must be recorded on a project approved form by the manager responsible for that project prior to the receipt and log-in of samples. Projects, and therefore samples which are not routine to the WWES laboratory, must have prior approval via the New Project Approval Form before samples may be received.

8.2 NEW PROJECT APPROVAL

The project approval form include the following information:

- Client name, address, and client contact personnel
- Anticipated due date of the report (i.e. report in client hands by _____)
- Compound names or computer test codes or group computer test code
- Project and sample comments
- Contract number or purchase order for project
- Instructions relative to the proper completion of the project
- Pricing information relative to the proper completion of the project
- Chain-of-custody requirements

- Specific report requirements
- Additional requirements such as rush, hazardous, labile

8.3 NEW PROJECT APPROVAL

If a new project will require support from the analytical facilities, that project must be approved by the laboratory supervisors and the laboratory manager prior to project pricing and sample receipt. Routine samples are those samples and analyses which are continuously processed by WWES, such as priority pollutant samples, microbiological samples, and drinking water samples.

Projects which are non-routine are those that may require special testing, or which request parameters not routinely run within the laboratory, special holding times, or rush turn around. Non-routine projects will require that a New Project Approval Form be completed which includes the signatures of all the parties involved with the project. For example, if specific physical testing is necessary, the supervisor of the physical testing facility and the laboratory manager will have to sign off on the form thereby agreeing, not only to the project content, but for the turn around, the report requirements, the detection limits and the quality control reports that may be necessary to properly carry out the project requirements. Projects and/or samples arriving at WWES which are non-routine in nature, and for which there is no signed Project Approval For,, will not be processed. In this case, the manager responsible for the non-routine project will be advised of the problem and will then explain to the client why the delay is necessary for the execution of testing before proceeding to obtain the necessary approvals. The Project Approval Form must be completed and signed by all parties prior to the start of log-in.

8.4 SAMPLE RECEIPT

8.4.1 Introduction

All samples will be received at the WWES facilities by the Sample Coordinator (SC). The job description for the Sample Coordinator is attached as Figure 10. It will be the responsibility of the SC to determine: a) whether or not the proper project sheet is available for the arriving samples; b) whether or not the samples require chain of custody; c) whether or not the samples are labile in nature and require immediate attention; d) the manner in which those samples will be split, preserved and stored or routed. It is the objective of the SC to insure that the receipt of all samples is consistent with the requirements of the WWES Manual and that all pertinent information relative to those samples is recorded. This information may be used in client reports, communicated to the laboratory or to the client and, in some cases, reported to a legal authority relative to Chain-of-Custody samples.

FIGURE 10

SPECIFIC RESPONSIBILITIES

The SC's duties and responsibilities shall include, but not be limited to:

1. Sample receipt.
2. Insuring that COC sample receipt includes shipper's signature on COC forms.
3. Inspection of sample shipping containers for presence/absence and condition of:
   a) custody seals, locks, "evidence tape", etc.
   b) container breakage and/or container integrity
4. Recording conditions of both shipping containers and sample containers (bottles, jars, cans, etc.) in appropriate logbooks or on appropriate forms.
5. Signing appropriate documents shipped with samples (i.e., Chain-of-custody record(s).
6. Verifying and recording agreement or non-agreement of information on sample documents (i.e., separate tags, Chain-of-Custody records, traffic reports, airbills, etc.) on appropriate forms and on the WWES project sheet.
7. Initiating the sample and project log-in procedures on appropriate laboratory documents and according to the WWES Log-in Procedures document, including the initiation of project files with sample control records.
8. Marking or labeling samples with laboratory sample numbers, as appropriate.
9. Placing samples and spent samples into appropriate storage and/or secure areas.
10. Controlling access to samples in storage and assuring that laboratory operating procedures are followed when samples are removed from and returned to storage.
11. Monitoring storage conditions for proper sample preservation such as refrigeration temperature and prevention of cross-contamination.
12. Returning shipping containers to the proper client or licensed disposal facility.
13. Providing for the splitting of samples into required aliquots, including preservation for each working station.

8.4.2 Examination of Shipping Container

Immediately upon receipt of a sample shipment at WWES, the SC will examine the shipping container (the container may be a box, a cooler, a styrofoam container, etc.) to ascertain and document the condition of the samples and to process Chain-of-Custody papers, where appropriate. The SC will record the condition of the shipping container, the identification of the shipper, the presence or absence of any seals on the container (if it is Chain-of-Custody), and the labeling which may include special instructions prior to opening the container. If the shipping container is damaged, a report will be sent immediately to the shipper and the lab supervisor (see Section 8.15.2, Problem Project Sheet).

8.4.3 Carrier Sign Off for Chain-of-Custody Container

Should the SC identify the shipping container as being a Chain-of-Custody container, the SC will attempt to have the carrier's representative sign off on the Chain-of-Custody papers which should be available either on the outside of the shipping container, or immediately inside. An example of a Chain-of-Custody record is attached as Figure 5, (Section 7). In the event that the carrier's representative is unwilling to cooperate in this fashion, the SC will identify, in the proper position on the Chain-of-Custody document, the shipment number, the date of receipt, and sign off, attaching a copy of the shipping log for that particular container.

8.5 EXAMINATION OF CONTAINER CONTENTS

Unless the shipping container contents are marked "hazardous" the SC will proceed to open the sample container. If the SC had not previously identified the project sheet appropriate for these samples, the SC will attempt to ascertain immediately the origin of the samples found in this container and obtain the appropriate project sheet. If a project sheet is not found, the SC will lock up the samples and notify the lab manager as described in Section 2.0. The SC will identify whether or not all the samples have arrived intact, whether or not the labels are intact and attached properly, and whether or not the samples have leaked in any fashion. The SC will also identify any shipping instructions, field instructions, or any other materials that may be present in the shipping container.

8.5.1 Chain-of-Custody Shipments

Should the SC identify the shipping container as a Chain-of-Custody project, the SC will immediately follow the procedure outlined in Section 4.0, "Chain-of-Custody Samples".

8.6 PROJECT VERIFICATION

The sample coordinator, having opened the shipping container and examined all the samples, will verify that the project sheet matches the samples, the number of samples received is consistent with the project sheet, and that the requirements identified on the project sheet are consistent with any paperwork obtained which will include the project sheet and any other documents in the sample container. The project files will be kept by the SC in a locked filing cabinet. If all required project information is not complete, the SC will fill out a Problem Project Sheet (see Section 5.2) and turn it over to the Project Manager.

8.7 LABILE SAMPLE DISTRIBUTION

Should the SC identify labile samples within the shipping container, (i.e. coliforms or nitrites) for which there is a very short holding time and a need to rapidly move the samples into the laboratory, the SC will make every effort to immediately log-in those samples. Should log-in be delayed, the SC will coordinate with the responsible analytical group in order to move the samples into analysis. The coordinated effort will included means by which the SC can label the samples after log-in and insure that the results correlate with the proper samples. The SC will provide computer generated sample identification to the responsible analytical group. It will be the responsibility of the SC, once labile samples have been distributed to the laboratory to insure that those samples are properly logged in and that they are labeled with properly sequenced numbers. The agreement that is made between the SC and the appropriate laboratory manage or laboratory supervisor will be based on the premise that the SC understands that he/she is ultimately responsible and will be held accountable for any samples that are lost in such a movement. Consequently, the SC will find the samples that are labile and apply the necessary labels.

If a shipping container is labeled "Hazardous", the SC will immediately notify the laboratory supervisor who will determine the extent of hazard and/or the manner in which the samples will be handled. The supervisor will involve the laboratory manager as needed in resolving questions of hazardous samples.

FIGURE 11

POSITION DESCRIPTION FOR SAMPLE COORDINATOR

GENERAL

The Sample Coordinator (SC) is responsible for the receipt, log-in, and storage of all client samples at WWES. The SC is responsible for the receipt, storage and custody of all Chain-of-Custody (COC) samples including distribution of COC samples to lab personnel per WWES COC procedures (section 4.0, WWES Log-in Procedure). In order to ensure the successful analyses of samples, it is critical that the SC obtain and communicate to Project Manager, lab supervisors, and lab personnel, all information necessary for the processing interpretation and reporting of all samples analyzed.

QUALIFICATIONS

High School Diploma and a minimum of 2 years of college or equivalent. A knowledge of chemistry and testing procedures helpful. Excellent verbal, written and organization skills, including a propensity for detail necessary for successful completion of job.

REPORTING RELATIONSHIPS

The SC will report to the laboratory manager. The SC will communicate closely with the Director and Project Managers to obtain project information.

8.8 CHAIN-OF-CUSTODY SAMPLES

8.8.1 Continuance of Log-In Procedures for Chain-of-Custody Samples

All samples in the possession of WWES under Chain-of-Custody (COC) procedures must be traceable from the time the samples are received at the WWES door (or collected by WWES staff) until results are reported and sample disposition has been determined from the client. For any samples that may be collected during enforcement investigations, under litigatory requirements, or evidentiary in nature, Chain-of-Custody procedures are required.

8.8.2 Examination of Container Contents

Although Section 8.4.2 under Sample Receipt discusses the thorough examination of container contents, the proper examination of a container which is involved in a Chain-of-Custody procedure is even more important. For example, should the sample labels be mismarked or a particular sample to somewhat strange in nature, it is necessary to note all observations and deviations from the project sheet. It is better to be overly observant than to allow possible anomalies to go unnoticed. It is the SC's responsibility to examine whether or not each of the sample containers are individually sealed, whether those seals are intact, whether a sampler's initials are on the seals, and whether or not the paperwork matches the contents of the package. In addition, the SC must note whether or not all the dates and times are consistent, and whether or not the sample description on the paper work matches the description on the sample container.

8.9 PROJECT VERIFICATION

In the same manner in which the examination of the container contents is critical to a COC project, the verification of the project is equally important. These project verification steps include not only the need to follow the requirements identified in Section 8.6, but also thorough examination of all aspects of the project and the consistency of all the paper work involved with those particular samples in that shipping container. It is also important that the SC place in the COC project file: the shipping document; a signed Chain-of-Custody document including the sign off from the shipper's representative (See Section 8.4.3); a copy of the project sheet; a copy of the Project Approval Form is appropriate; a copy of the filed sampling report if appropriate; and originals of all paperwork received for the project. The COC project file is kept in locked storage in the possession of the SC.

8.10 CHAIN-OF-CUSTODY LOG-IN

The log-in procedure identified in section 8.15 titled "Log-in", is followed in the same manner for Chain-of-Custody samples with a few modifications. Those areas which are changed are addressed in the following sections:

- Sample Storage
- Project Files
- Laboratory Access
- Data Storage

8.11 CHAIN-OF-CUSTODY SAMPLE STORAGE

All samples received under Chain-of-Custody procedures will be kept under locked storage and will be distributed for analysis to the laboratory only when the analyst has signed for the samples on the form shown in Figure 6, (Section 7). The SC or a designated representative will provide access to COC storage. Records of movement of all COC samples within the lab facility must be recorded.

8.12 CHAIN-OF-CUSTODY PROJECT FILES

All Chain-of-Custody project files will be kept in a project folder in a locked cabinet with all related documents and paperwork relative to those files.

8.13 MAINTENANCE OF LAB CUSTODY

Laboratory custody must be consistent with all the Chain-of-Custody requirements from the beginning of sampling to the final report. To this end, every analyst requiring access to the Chain-of-Custody samples will go to the SC for access to the COC locked sample storage. The SC will insure that the analyst signs for the receipt of all COC samples on the form shown in Figure 6, (Section 7) and that the analyst returns and signs in those same samples on the same day for which they were signed out. This documentation, after the completion of all analyses, will be placed in the locked Chain-of-Custody project file by the SC.

8.13.1 Sample Custodian

The COC sample custodian at WWES will be designated as the Sample Coordinator (SC). The SC is responsible for following the COC requirements outlined in these procedures for all samples received at WWES.

8.13.2 Lab Custodial Responsibilities

It will be the responsibility of every analyst signing for a Chain-of-Custody sample or samples to insure that; a) these samples are kept in a minimum access

facility; b) they are within their possession during the particular period during which they are being analyzed; and c) the analyst returns those samples to the Chain-of-Custody lockup in the manner prescribed. The analyst will sign out and return the samples to COC lock-up on the same day. The analyst will be using the SC as the sample custodian for all COC samples. Due to the legal implications for the client of breaking the COC procedures and possibility of legal action that could be taken against WWES, errors in the execution of Chain-of-Custody procedures will not be tolerated.

8.14 CHAIN-OF-CUSTODY SAMPLE DISPOSAL

All samples received for COC procedures will be stored in the WWES COC lock-up facilities until a final report is issued. It will be the responsibility of the Project Manager, in cooperation with the SC, to obtain information from the client relative to the length of time the COC samples will be stored. It is anticipated that for long term storage, i.e. more than 30 days, the client will reimburse WWES ' n appropriate rate for keeping completed samples under Chain-of-Custody procedures. No Chain-of-Custody samples may be discarded until written permission is received from the client relative to disposal of those samples.

8.15 LOG-IN

8.15.1 Introduction

After the Sc has inspected the shipping containers, the project sheets, the samples and any documentation required in Sections 8.4 and 8.8, the SC will insure that all pertinent information is entered on the project sheet. There are specific areas of the project sheet that are to be completed by the SC, i.e., date and time received. The WWES project sheet is included as Figure 2, (Section 7).

Minimum information required for log-in include:

- Client's name and Client contact, as well as client #, is assigned.
- The due date
- The analytical test or test codes or group tests
- Specific project comments
- Contract requirements
- Contract number
- Pricing if necessary
- The approval for non-routine projects
- Chains-of-Custody, if required
- Specific report requirements

8.15.2 Project Problems

If any of the information identified in sub-section 8.15.1 is missing, the SC will immediately notify the Project Manager, via a Problem Project Sheet, Figure 4, (Section 7) of the discrepancy. The Project Manager will make all reasonable efforts to insure that the answers are provided to the SC immediately.

Simple Project Sheet deficiencies such as client number, extra comments, or the contract number, should not prevent log-in. The SC will proceed with log-in addressing the unknowns as subjects that must be changed or modified once the information is received. It is the responsibility of the SC to log-in all samples as received at WWES whenever possible.

8.15.3 Samples on Hold

When there is a considerable amount of inadequate information on a project sheet, i.e. a missing test, or broken samples, the entire project will be placed on hold until the information is available or the corrective actions have been taken to insure that NSF is not held responsible for a poorly handled project. The SC will notify the Project Manager via a Problem Project Sheet as to the hold status of the project and the reasons for the hold. The Project Manager will make every attempt to quickly identify the necessary actions that will be taken for those samples or the remaining samples for that project. The Project Manager may approve log-in of the remaining samples for a portion of the project in order to insure that the project progresses. Projects that are placed on hold will be locked in a "project hold" area, (like the Chain-of-Custody sample storage area) so that those samples are not lost or confused within the system. The SC will insure that those samples are retrieved and logged in as soon as the appropriate changes have been made and the samples are freed for log-in.

8.15.4 Handling Labile Samples

All samples received by the SC that are labile in nature, i.e. coliforms, need to be logged into the facility in a very rapid fashion in order that they may e attended to within the analytical holding time. The most labile of all samples are the microbiological samples, which must be forwarded to the micro lab as soon as possible. The SC and the Project Managers responsible for micro work will attempt to insure that appropriate information is available to the SC in order that the SC can assign numbers for all labile samples. These numbers can be assigned in advance and samples may be logged into the system as soon as they are received. Samples such as nitrites, which are labile but have a somewhat longer holding time, will usually be logged into the system like normal samples. However, slow shipment or other problems may require the lab to initiate the analyses immediately. In such a case, assuming a project sheet was initiated in

advance o sample receipt, the SC can assign laboratory in an expedient fashion. The SC will make all efforts to insure that samples move through the laboratory in a timely fashion when holding times are of utmost importance to the proper completion of the analytical requirements.

8.16 COMPUTER LOG-IN

It is anticipated that all samples received at WWES will be logged on to the computer by the SC. The computer assigns a sequential number to every sample. Additional codes such as the month and the year of the samples may be added in front of the sequential number for continuous identification of these samples. The SC will have the computer generate these sequential numbers for each sample in every project. A project identifier will be printed on the labels which are attached to every sample and every aliquot of a sample.

8.17 SAMPLE SPLITTING FOR THE CHEMICAL LABORATORY

The WWES Project Manager will attempt to insure that all samples received at the WWES facility are received in the appropriate containers with the correct preservatives (Samples which must be split at log-in are subject to added error). The labels and the appropriate preservatives are depicted in Figure 12.

8.17.1 Bottles and Preservative Requirements

The WWES analytical facility has a series of bottle and preservative requirements that must be met before the log-in of samples into the laboratory. In the event that WWES is unable to provide sample bottles, or circumstances prevent the splitting of samples in the field, the SC will provide sample splitting services. These services will include taking the sample as received and subsampling it into the appropriate bottle and preservative requirements as set forward on the attached list of bottle and preservative requirements.

8.17.2 Inorganic Samples

The SC will insure that sufficient sample volume is available before initiating the splitting of a sample. If uncertain, the SC will involve the laboratory supervisors in order to insure that all areas of the lab have sufficient samples. In the event that sufficient samples does not exist, the SC will identify the sample as a problem and will notify the Project Manager immediately for resolution. The sample will be logged in only after a resolution has been reached.

8.17.3 Organic Analysis

When a bulk sample arrives for organic/inorganic analysis and sufficient sample exists, the SC will transfer the sample to the organic preparation supervisor who

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Date Requested: / / Date Due: / /
Dispatched By: _____
Project: _____
Project Manager: _____
Project No: _____
Location: _____

Sample Inventory and Master Bottle Packing List

Sample Locations	Sample Number	Sample Sub-Portions-Preservative and Tagging Codes																							
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						

Indicate Sample Sub Portion with an X
Multiple Sub Portions for the same Bottle Type can be identified by Entering the Number Needed

NO.	DESCRIPTION	PRESERVATIVE	TAG COLOR	FILTERED
	Waters			
1	40 ml Vial for Purgeable Organics	1+1 HCL Yes / No Cool to 4° C	Yellow	
2	1000 ml Amber Glass Non Purgeable Organics	Cool to 4° C	Salmon	
3	ml Plastic - Non Preserved	Cool to 4° C	Green	
4	ml Plastic - Nutrients	pH < 2.0 w/H_2SO_4	Blue	
5	ml Amber Plastic - Cyanides	pH to > 12 w/NaOH	Light Blue	
6	ml Plastic - Metals	pH to <2 w/HNO_3	Red	
7	1000 ml Glass - Oil & Grease / TPH	pH to <2 w/H_2SO_4	Dark Blue	
8	125 ml Whirl Pac Bag / Bottle Bacteria	Cool to 4° C	Brown	
9	500 ml Glass - Sulfide	0.5 ml Zinc Acetate + 0.5 ml NaOH to pH >9	Light Green	
10	250 ml Amber Glass - TOX	pH to < 2 w/H_2SO_4 Cool to 4° C	Lilac	
11	40 ml Amber Glass - TOC	pH to < 2 w/H_2SO_4 Cool to 4° C	Pink	
12	2000 ml Plastic - Radiological	pH to < 2 w/HNO_3	Gray	
13	500 ml Amber Glass - Phenols	pH to < 2 w/H_2SO_4	Brown	
14	250 ml Amber Glass - Formaldehyde	Cool to 4° C	Orange	
	Soils			
15	ml Wide Mouth Plastic	Cool to 4° C	White	
16	ml Wide Mouth Amber Glass	Cool to 4° C	Manilla	
17	125 ml Vial for Purgeable Organics in Soil	Cool to 4° C	Light Yellow	
18	Other			

Figure 12

will split the organic aliquots and return all aliquots to the SC. The remaining sample will then be returned to the SC who will split off the inorganic aliquots into the proper preserved containers.

8.17.4 Solid Samples Splitting

When solid samples, such as sediment or soil, are to be received at WWES, every attempt will be made by the Project Manager and field sampling personnel to insure that two samples are provided as replicates for the appropriate tests. One of these samples will be assigned to the organic facility; the other will be assigned to the inorganics facility. If only one sample is received and if organic analyses are required, the organics preparation chemist will be responsible for the initial splitting of the sample. Solid samples will be made homogeneous by either one or all of the following manners:

- Stirring especially when volatile organic analytes are required
- Air Drying and Grinding
- Particle separation (Sieving)
- Quartering by ASTM Procedures

The lead organic chemist and the SC are responsible for the decisions on how a solid sample will be split. Problems or concerns which may arise on a solid sample will be addressed to the Project Manager and the laboratory manager for resolution. After the organic portions have been removed or split, the remaining sample will be provided to the inorganic facilities for any further splitting they deem necessary.

8.18 SAMPLE LABELING

All samples received at the WWES facility will be labeled by the SC at the time of log-in. These labels will include information such as the requested sample number, the client number if supplied, the contract, the WWES project number, and/or the client. It is anticipated that sequential sample labels will be provided by the computer after the SC has logged the project into the computer.

8.19 DISTRIBUTION AND STORAGE

Logged samples will be taken by the SC to the appropriate walk-in cooler for cold storage or to the room temperature storage area indicated for metals.

COC samples are stored as set forth in Section 4.0.

8.20 PROJECT FILES

8.20.1 Routine Project Files

The SC will obtain a manila folder and label that manila folder with the name and number of the project. The folder will indicate the WWES project number, the WWES contract number, and Chain-of-custody if applicable. With the agreement of the laboratory supervisor (lead), the project manager, and the laboratory manager, a particular project folder may include a series of projects logged in under sequential numbers. An example would be a daily log-in for the same project for a week or month before a new project folder is generated. It is, however, the responsibility of the SC to insure that all logged projects are filled in a project file folder.

8.20.2 Chain-of-Custody File Folder

The SC, upon logging in any Chain-of-Custody project, will provide the same type of manila folder project file, as discussed in Section 5.7.1, for each project. However, the project folder will be maintained in the locked Chain-of-Custody file and cabinet and will be kept by the sample coordinator.

8.21 SAMPLE STORAGE

8.21.1 Non Chain-of-Custody Storage

The SC, after completing all the log-in processes of various samples connected with a particular project, will store the samples in the designated areas in the WWES laboratory.

- Routine Water and Solid Samples: Samples which need to be refrigerated will be stored in the walk in facility designated for all routine water and soil samples.
- Routine Volatile Water and Solid Samples: All these samples will be placed in the designated VOA refrigerator(s) located within the analytical facility. No other samples or standards may be stored in the VOA refrigerator(s).
- Routine Water and Solid Samples for Metal Parameters: The preserved water samples and solid samples, which are not preserved, may be stored on shelves designated for the metals analysis.
- Odoriferous and Hazardous Samples: These samples will be stored in a hooded facility within the laboratory which is designated for Odoriferous and hazardous samples. These samples will be identified to the lab

personnel and noted on the log-in procedures in order to insure that the lab personnel are aware of the problems with these samples.

8.22 CHAIN-OF-CUSTODY SAMPLE STORAGE

All samples that are involved as physical evidence in a legal procedure or simply identified as Chain-of-Custody will be handled under certain procedural safeguards. These safeguards have been tentatively identified in section 4.0 but for purposes or reiteration are again addressed below:

NOTE: For any legal proceedings, the court must be shown that the laboratory is a secured area, that all samples have been stored in a secured fashion, and samples can be accounted for at all times.

8.22.1 Chain-of-Custody Water and Solid Samples

All samples of this nature will be stored within the locked confines of the Analytical Laboratory. Access is only available to authorized personnel.

8.22.2 Water and Soil Samples for Metals

8.23 GENERAL LAB SECURITY

Access to the WWES lab will be handled in a secured fashion restricting entrance only to those people designated as having access to the laboratory facilities. Restricted access applies to all areas in which samples are stored or analysis takes place. It will be the responsibility of all the analysts, as well as the supervisors and the SC, to insure that the safeguards employed, including locked doors and limited access, are followed and maintained at all times.

9.0 DATA HANDLING, REPORTING, RECORDKEEPING AND VALIDATION

9.0 DATA HANDLING, REPORTING, RECORDKEEPING AND VALIDATION

There are two significant aspects of any analytical procedure:

- The selection and use of a method appropriate for the analyte and matrix
- The collection, control and interpretation of the data generated.

Encompassing these two components is the Quality Assurance program. The QA program provides means by which method selection can be validated, the method can be controlled and the appropriate data generated, displayed and reduced.

The following sections deal with error, data handling, data validation, data reporting and data recordkeeping.

9.1 ERROR: IT'S NATURE AND SIMPLE STATISTICAL CONCEPTS

9.1.1 Random Errors

Repeated analysis of identical aliquots of a homogeneous sample does not give a series of equivalent results. The results will differ among themselves and they will be more or less scattered about some value. The scatter can be attributed to random error, so named because the prediction of the sign or magnitude of the error of any particular result is not possible at the time of analysis.

One therefore, says that each result must have an uncertainty attached to it, and can be regarded only as an estimate of the true value. Generally that estimate will differ from the true value. Random errors are caused by uncontrolled and/or uncontrollable random variations in factors which affect analytical results, i.e. variations in the volumes of the reagents added, variations in the concentrations of reagents, variations in the time allotted for the chemical analysis, a contaminated glassware, poor quality reagents, instrumental fluctuations. Among the various texts that are available discussing errors, the terms repeatability, reproducibility and precision have been used to denote the scatter of results. The term "precision" will be used throughout this manual and is the most common term used for random error in this country and especially by the EPA.

Precision does improve as the scatter among results becomes smaller. All analytical results have random error present which necessitates statistical techniques to evaluate the results and to provide correct inferences of the true value of the result.

9.2 SYSTEMATIC ERRORS

Systematic errors are indicated by the tendency of results to be greater or smaller than, the true value. It is necessary to take care in exactly defining systematic error because

the analysis is also subject to random error. The mean of n analytical results on the same sample approaches a definite value u as the number of results increases indefinitely. When u differs from the true value Tau results are said to be subject to systematic error of the magnitude B, wherein B is equal u minus Tau. Bias is the term used synonymously with systematic error and will be used in that fashion throughout this manual. Analytical methods, which are subject to interferences from substances present in the sample, or methods that only recover a fraction of the material present are an example of systematic error.

It is impractical to make an indefinitely large number of analysis on a single sample in order to determine the true value of u is known. At the same time a practically obtained value for a sample that is based on minimal analysis is subject to random error, so that the experimental estimates of bias will also be subject to random error. Therefore, statistical techniques are also required when bias is to be estimated.

The basic difference between random and systematic error is that, in principal, the latter may be predicted so that a correction can be made to eliminate its effect. An example of this allowance can be accounted for in the effect of fluoride in the determination of aluminum by absorbance measurements. This effect is overcome by adding to the calibration standards an amount of fluoride equal to the fluoride content of the sample. The added fluoride in the calibration standards then eliminates the systematic error of fluoride interference. However, it must be recognized that the complete elimination of systematic error may require such detailed knowledge of the properties of the sample that the correction of the analytical system is impractical and would in fact increase the amount of random error. Thus, in all applications where unbiased results are necessary, the approach to be used is to devise and use analytical systems capable of giving results which have negligible systematic error.

9.3 TOTAL ERROR

Some analysts use the term accuracy to denote only systematic error. The term accuracy as applied in this manual will denote total error of the results. In other words, accuracy represents the combined systematic and random error of the results and, therefore, the accuracy of an analysis improves as the total error becomes smaller. For the purposes of visually seeing random and systematic error, Figure 6-1 should be referred to for any easy identification of the various types of error.

9.4 STATISTICAL TECHNIQUES

Statistical techniques are essential to the measurement of analytical error. This manual and this section recognize that many analysts have had little experience with statistical technique. This section is, therefore, written in such a way as to explain simple but basic concepts of the statistical approach and to describe the particular techniques most commonly required in dealing with analytical errors. There are a large number of text

books dealing with statistics and this particula- section does not attempt to replace these books. The intention is merely to present the essential aspects in the simplest manner possible. Certain approximations have been used when considered appropriate and no previous knowledge of statistics has been assumed. Should the analyst be interested in consulting additional texts for a more rigorous and detailed treatment of the subject, he is referred to the references at the end of section 9.0.

Analysts who are unfamiliar with statistical approach, may find this section on first glance rather complicated. In order to understand statistics for the QC function, it is important not to be put off by the first impression.

The fundamental statistical concepts are essentially simple and equivalent to the intuitive common sense, or perhaps scientific approach, adopted by any good analyst.

9.4.1 Random Error Distribution

If the results from the analysis of numerous aliquots of a homogeneous sample are plotted on a histogram, it is generally found that the proportion of the results deviating from the mean increased, i.e., as the deviation of the results from the mean grows broader. In other words, the probability of obtaining a random error of a given size decreases as the size of the error increases. The basis of statistical techniques is to quantitatively estimate the probabilities of errors of different sizes so that one can deduce the probable random error of a particular analytical result. If the analyst were to increase the number of analysis of a single sample indefinitely, and the size of the intervals used for plotting the histogram were decreased, the latter would tend to smooth the curve. This limiting curve is the frequency distribution of results and defines a relationship between the magnitude of the result and the probability of obtaining such a value. Throughout this manual, it will be assumed that the analytical results follow the normal distribution which is defined by the following equation:

$$p(x) =$$

Where: = the mean of all the conceptionally infinite number of results.

= the standard deviation of results

$p(x)$ = the probability density which is interpreted by noting that the probability of obtaining a result between the values a & b is the area of the curve between those values.

and this interval can be evaluated given the equation for P(X).

The peak of this distribution curve occurs at x=u, the theoretically perfect mean established by an infinite number of results. The width (which is indicated by the

scatter results) is determined solely by the standard deviation of the test. For example, 95% of the area under the curve, i.e. 95% of all results, is enclosed within the limits plus or minus 1.96. Such properties allow limits for the uncertainty of an individual analytical result to be calculated. Taking the current discussion, for example, on no more than 5 occasions in one hundred will the result differ from the mean u be more than 1.96. Thus, an analyst may attach to a result limits that define the range in which the true mean is expected to lie. The statement, R-1.96 is less than u which is less the R+1.96, is an accurate statement on 95% of all occasions. "R" in this particular case would stand for the result. By referring to texts on statistics, there are statistical tables which included a tabulation of areas enclosed between specific limits as an analyst might want to define them. It should be noted that the distribution is always symmetrical about the mean. In other words, if one is using the 1.96 levels 5% of the results will be outside of the range of u +/- 1.96, but only 2.5% of all results will exceed u + 1.96 and 2.5% of the results will be less than u - 1.96.

Focusing this into a discussion more pertinent to the laboratory and, perhaps more viable with respect to occurrences within the laboratory, let us discuss the rare exception in which an analyst is taking 20 tests on a particular sample using the 1.96 level. Considering that 5% of the results will lie outside that level, the analyst has 1 chance in 20 of missing the true value outside the stated confidence range. At the same time one can decrease this chance by increasing the allowable range. For instance, if the range is R =/- 2.58 the results will be included on 99% of the occasions or 99% of the tests. However, by increasing the confidence limit, one is also increasing the uncertainty in the true value. In this case, uncertainty can be decreased by taking the mean of several analytical results or by decreasing the value.

These statistical concepts allow valuable quantification of the random error of an analytical result and emphasize that decisions, based on the significance of the result, have some risk of being wrong. Knowledge of the standard deviation, of the results is, therefore, vital in reaching objective decisions. Use of the standard deviation will be explained in the following sections dealing with data handling and validation.

9.4.2 Data Handling, Reporting, Recordkeeping

A flow diagram, Figure 1, delineates the original and procedural steps in data generation.

The initiation of an analysis starts with the completion of a project approval form. The information is computer entered. The computer entry internally creates a report form and inventories the analysis by parameter or compound. The computer entry function of all analytical work requests is a shared responsibility

of the sample coordinator and data coordinator. A copy of the analysis request form is manually inserted into a three ring binder notebook for laboratory reference use. The maintenance of the laboratory job reference notebook is a responsibility of the sample coordinator. The group leader/supervisors requests from the data coordinator (D.C.), the computer generated analytical bench sheets for a given parameter each morning or the prior day. The samples and parameters testing sequence is dictated by a weekly work schedule. The weekly work schedule is developed manually each week by the group leaders/area supervisors and approved each week by the laboratory manager. The schedule is developed from a computer printout that inventories and ages by project job or parameter. Contractual due dates and sample holding times are the compliance criteria by which all schedules are judged.

The bench sheets examples are shown in Figure 7, 8, 9. The bench sheets identify to an analyst the proper samples to analyze that day. The analyst lab notebook and the bench sheets constitute the two raw data reporting locations. The content of the laboratory notebook is defined in an earlier section, 7.3.7. The analyst completes the benchsheet information, attaches a drawn calibration curve and follows the analytical sample sequence identified in section 10.0. The analyst identifies which sample(s) were utilized for precision and accuracy determinations. The analyst will assess the data set as being in control or not. The assessment will be described in the data validation section to follow. The analyst will submit to respective group leaders or supervisors all of the above-mentioned data and a written statement that the data set is in control for their review. An approved data set is signed off and the group leaders/supervisors transfer the approved data to all appropriate worksheets in the laboratory job reference notebook. The bench sheets and calibration curves are permanently stored. The last entry into the worksheet constitutes a completed project subject to computer generation of a preliminary report. The group leader/supervisors provide the DC with the approved worksheets for computer entry and preliminary report generation. The remaining activities related to preliminary report, final report generation and review and project filing are identified in this manual under sections 7.3.14, 7.3.15 and 7.3.16 respectively.

9.5 DATA VALIDATION

The data validation process includes a set of computerized and manual checks at various appropriate levels of the measurement process.

The data validation process starts with the laboratory analyst. The analyst verify in their lab notebook that all method specific operational parameters are utilized or met. This information is specifically documented in all instrument logbooks. The analyst then verifies that the calibration of the equipment is linear and documents this in the instrument logbooks. If the operating parameters of a particular method are modified, it

should be written in the analyst lab notebook and approved via signature by the group leader/supervisor in the lab notebook. A non-calibrated system must be identified by the analyst and corrections made to achieve calibration prior to sample analysis.

The generation of sample data by an analyst will include the generation of quality control data for each sample set. The monitoring of method blanks, sample spikes, method spikes and sample duplicate analysis is accomplished by the utilization of Schwart Quality Control Charts. All quality control data is entered on the precision and accuracy data summary form, Figure 11a. The analyst computes the data precision and accuracy and compares the computed value to the acceptance intervals identifies on the form for that parameter, method, and matrix. The computed value will be determined in control if it lies within the acceptance interval. If the computed value is deemed out-of-control the data set is not submitted for supervisor approval but is brought immediately to the attention of the supervisor and quality assurance officer that an out-of-control condition exists. Jointly, a review is conducted to determine the cause(s) and conduct corrective action. The data set is rerun once the corrective actions have taken place and the new data reviewed as stated above.

The DC receives all the completed precision and accuracy data summary forms and enters the data into the laboratory quality control computer system. The system produces summary reports each day of all quality control data generated for review by the quality assurance officer. The computer system also generates all Schwart Control Charts for method blanks, method spikes, sample duplicates and sample spikes. The charts are permanently maintained and reviewed each week by the group leader/supervisor and the quality assurance officer. The weekly generated charts provide an accurate review of all recently (last 30) qc data points and allows the monitoring of data trends or other anomalies to the system.

10.0 GENERAL QUALITY CONTROL PRACTICES

10.0 GENERAL QUALITY CONTROL PRACTICES

The Quality Assurance/Quality Control practices at WWES are based on several of the following government guidelines:

- "Handbook for Analytical Quality Control in Water and Wastewater Laboratories "EPA 600/4-79-019, March 3, 1979
- The Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act 40 CFR; July, 1990.
- Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples" EPA 600/8-80-038 June 1980.
- ASTM
- Test methods for evaluating a solid waste; USEPA SW-846; Third Edition, Revision 0.

10.1 The quality control types normally analyzed during sample analysis includes the following: Initial Calibration Blank (ICB), Initial Calibration Verification (ICV), Method Preparation Blank (MPB), Laboratory Control Sample (LCS), Sample Matrix Spike Duplicate (MSD), Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB).

10.2 The frequency of which these QC types are performed during the analytical run is usually stated within the analytical method. The general frequency over-all of these types, and their respective order within the analytical run is as follows: (following instrument calibration).

Type	Frequency
Initial Calibration Blank	1-per batch
Initial Calibration Standard	1-per batch
Sample #1	---
Sample #2	---
Sample #10	---
Method Preparation Blank	1-per batch
Laboratory Control Sample	1-per batch
Sample Matrix Spike	10%
Sample Matrix Duplicate	10%
Continuing Calibration Blank	10%
Continuing Calibration Verification	10%

Any high level concentrations of analyte will be followed by a blank.

10.3 The level of internal laboratory quality assurance effort for the following is divided into 4 different categories:

1. Routine Analytical Services - (RAS). No special reporting requirements are required.

2. Reportable Analytical Services - (REP). For this type, batch quality control is reported for all analytes.

3. Special Analytical Services - (SAS). Each matrix type for a particular submittal will have internal QC performed on these particular samples at the appropriate method frequency.

4. Quality Assurance Project Plan - (QAPP). This level of QC encompasses all aspects of the SAS type with full data deliverables similar to CLP reporting packages.

10.4 The fundamental QA objective with impacting accuracy, precision and sensitivity of laboratory analytical data is to achieve the QC acceptance criteria established for each analytical method and matrix type.

The control limits established for each method are based on $\pm$ 3 standard deviations from the analytical mean. Also encompassed are method advisory limits if provided within the analytical methodologies.

The standard operating procedures that would lead to an outlier being identified and the resulting corrective actions is described in section 9.0, Data Reporting, Validation and Handling. In general, if an out-of-control result occurs the analyst will identify it as such and report the occurrence to the Group Leader and/or Area Supervisor. The Group Leader and/or Area Supervisor will review the data with the analyst to identify the problem, implement a corrective action(s) and then re-analyze the sample(s). The Group Leader and/or Area Supervisor will report the out-of-control occurrence to the Quality Assurance Manager that day in writing (Figure 13). The corrective action(s) will be identified in the analyst notebook and in writing to the QA Manager.

FIGURE 13

Analytical Quality Control Occurrence Report

Parameter: _____

Method: _____

Date: _____

Analyst: _____

Description of Occurrence:

_____

_____

_____

Analysis of Occurrence:

_____

_____

_____

_____

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_____

Disposition of Data:

_____

_____

_____

_____

_____

_____

WW Engineering & Science
A Summit Company

10/15/93

RMT
744 HEARTLAND TRAIL
MADISON, WI 53717-1934
ATTN: MR.MICHAEL SCHMOLET, P.E.

RE: FORD ALLEN PARK CLAY MINES

JEFF HARTLAND ASKED THAT I SEND THIS QA/QC DOCUMENT TO YOU.

PLEASE CONTACT ME IF YOU NEED ANY ADDITIONAL INFORMATION FOR YOUR PROJECT.

SHAR HOPP
WW ENGINEERING & SCIENCE
313-628-8150

NET Inc.
Quality Assurance Plan

NATIONAL
ENVIRONMENTAL
TESTING, INC.

NET Inc.
Quality Assurance Plan

Prepared by and property of:

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This is copy 2 of 50 copies.

SECTION 2

Introduction and Table of Contents

National Environmental Testing, Inc. (NET) currently operates several independent laboratory divisions throughout the United States. Services include multimedia analysis for metals, extractables and volatile organic compounds, conventional pollutants, asbestos and industrial hygiene analysis and sampling.

NET's Quality Assurance Plan (QAP) is based on the philosophy that quality is the key to maintaining leadership in the analytical laboratory field. We are committed to providing our clients consistently high quality services.

Quality Control is defined as the program applied to routinized systems (ie. systems composed of methods, equipment, materials and people) in order to evaluate and document the ability of a function, activity or person to produce results which are valid within predetermined acceptable limits. Quality Assurance is a planned system of activities whose purpose is to provide assurance to both the user and producer of the service that the quality control program is actually effective.

This document describes the essential elements of a Quality Assurance Program at NET and the quality control procedures utilized by NET to ensure a national standard of quality at all laboratories.

Table of Contents

SECTION 3

Project Description

INTRODUCTION AND SCOPE

NET believes that quality is the key to maintaining leadership in the environmental analytical industry.

The Quality Assurance program includes a Quality Assurance Plan (QAP), Quality Assurance Objectives and the systems for meeting those objectives. Also, the QA program includes Standard Operating Procedures (SOPs) and a National Quality Assurance Program (NQAP).

NET, Inc. provides Divisional, Regional and Corporate Management structure, Laboratory Information Management Systems (LABSYS), state-of-the-art laboratory instrumentation and facilities, and training programs for their employees.

QUALITY ASSURANCE POLICY STATEMENT

NET subscribes to the following policies as it's standard of quality in it's analytical program:

- It is our policy to maintain a national QA program throughout all NET laboratories, thereby providing our clients with consistent data of known high quality;
- It is our policy to communicate the scope and content of our QA program internally to our employees and to train each employee in the application of our program;
- It is our policy that no data will be reported to our clients that has not met our full QA requirements;
- It is our policy to remove from commercial offering any analysis offered by a NET laboratory when that laboratory fails to demonstrate it can consistently perform the analysis to NET's standard of quality based upon NET's Interlaboratory Testing Program; and
- It is our policy to strive for resolving to the client's satisfaction any questions concerning the validity or accuracy of analytical data reported by NET to the client.

SECTION 4

Organization and Responsibility

The main objective of the Divisional Quality Assurance Plan is to ensure that the Auburn Hills Division generates data of high quality. NET-Auburn Hills' Quality Assurance Plan has been developed to identify and implement policies and procedures to improve data quality. Also NET-Auburn Hills maintains all necessary records to document the division's performance.

The success of this Quality Assurance Plan requires the cooperative efforts and support of all personnel: Divisional and Corporate. The primary responsibility for data quality rests with the analyst in performing frequent and regular quality control checks on the work he or she does. This program is designed to support and coordinate these efforts at the bench level. The organizational structure related to quality assurance is shown on Figure 4.1 and specific responsibilities related to quality assurance are as follows.

Assignment of Responsibilities

The Analysts shall:

- Adhere to analytical and QC protocols prescribed by approved Standard Operating Procedures (SOPs) and Quality Assurance Plan/Quality Assurance Project Plan (QAP/QAPP);
- Review analytical QC data on a daily basis;
- Correct out of control analysis if possible; otherwise, seek the supervisor's help immediately; and,
- Suggest improvements in methodologies to supervisors and the Quality Assurance Coordinator. These improvements, if approved, will be incorporated into SOPs.

The Supervisors/Project Manager shall:

- Train new analysts in methodologies using regionally approved SOPs;
- Ensure compliance with approved SOPs, and QAP/QAPPs, including quality control measures prescribed;
- Investigate and assist the analyst in correcting an out of control analysis and document the investigation to the Division Manager and the Division QA Coordinator;
- Review and evaluate data produced by analysts prior to reporting;

- Communicate with other NET supervisors with similar areas of responsibilities;
- Guarantee that sample holding times are met or immediately notify the Project Manager if this cannot be done; and,
- Write SOPs as needed ensuring that they are representative of how the procedure is done in the laboratory, technically correct, complete, and of sufficient detail to serve as a training document.

The Quality Assurance Coordinator shall:

- Administer the National and Divisional QA Programs;
- Assist in the revision of the Divisional QAP and in the development of SOPs especially as related to quality control;
- Serve as a repository for the original copies of SOPs and the QAP and control the distribution of these documents and maintain a record of revision numbers and review dates for the QAP and QAPPs.
- Assist in the writing of QA Project Plans (QAPPs), ensure that they are complete and accurate with regard to regulatory requirements, and determine that the laboratory can meet the requirements set forth in the QAPP; maintain a copy of each QAPP and distribute a copy to the Technical Director of Quality Assurance;
- Assist in the implementation of the NET Interlaboratory Testing Program;
- Evaluate quality control processes and documentation throughout the laboratory;
- Conduct and assist in inter- and intradivisional audits and serve as QA support to division managers in external audits;
- Work closely with the Division Manager and the Technical Director of Quality Assurance to resolve quality related issues;
- Assist the Division Manager in identifying areas requiring corrective action and defining appropriate corrective actions. Determine that the corrective action has been properly documented and that a copy has been submitted to the Technical Director of Quality Assurance;

- Serve as a repository for all audit and performance evaluation results and for certification and licensing documentation. Submit copies to the Technical Director of Quality Assurance, and;

- Maintain current training files on all technical personnel.

The Division Manager shall:

- In the temporary absence of the Divisional QA Coordinator, assume all responsibilities of the Divisional QA Coordinator position;

- Ensure that the operational requirements of this Plan and supporting programs are met;

- Manage the on-going requirements of Quality Assurance and Quality Control activities through Project Managers, Supervisors and Divisional QA Coordinator;

- Edit, approve and implement SOPs, QAPs and QAPPs; ensure that these documents are complete, technically correct, accurately reflect what is done in the laboratory and meet NQAP and any applicable regulatory requirements;

- Coordinate analysis and reporting of ITP samples and provide written notice to the Technical Director of Quality Assurance and the Corporate QA Director if an analysis the Division normally performs cannot be conducted on a particular ITP sample;

- Ensure that appropriate corrective action is taken to address analyses identified as requiring such actions by internal or external performance or procedural audits;

- Review and submit corrective action reports to the Technical Director of QA;

- Have in place a system to ensure that sample holding times are met;

- Ensure that all analysts and supervisors have received adequate training to properly carry out the duties assigned them;

- Ensure appropriate laboratory certification, contract approvals and the analysis of Performance Evaluation (PE) samples necessary to satisfy certification requirements are properly managed;

- With the Project Manager, ensure that analysts and supervisors know any client specific reporting and QC requirements prior to sample arrival in the laboratory; and

- Represent, or designate an alternate individual to represent the Division during client and/or regulatory audits, with QA support as needed from the Division and/or Regional QA personnel.

The General Manager shall:

- Direct Quality Assurance Programs;
- Ensure that sufficient personnel resources are available at the Division level to implement this plan;
- Require Divisions to comply with and provide input on SOPs and QAP/QAPPs used within NET Inc;
- Remove analyses from Division product lines as outlined in the National QAP; and,

The Director of Data Information Systems shall:

- Assist the Divisions, and Corporate office in implementing specifics of this Plan when computer resources are employed as directed by the President; and,
- Coordinate the computer transfer of SOPs and QAP/QAPPs among the Divisions and Regions. He/She shall design and provide uniform directories, subdirectories and file nomenclature for these documents at every NET location.

The Director of Data Quality shall:

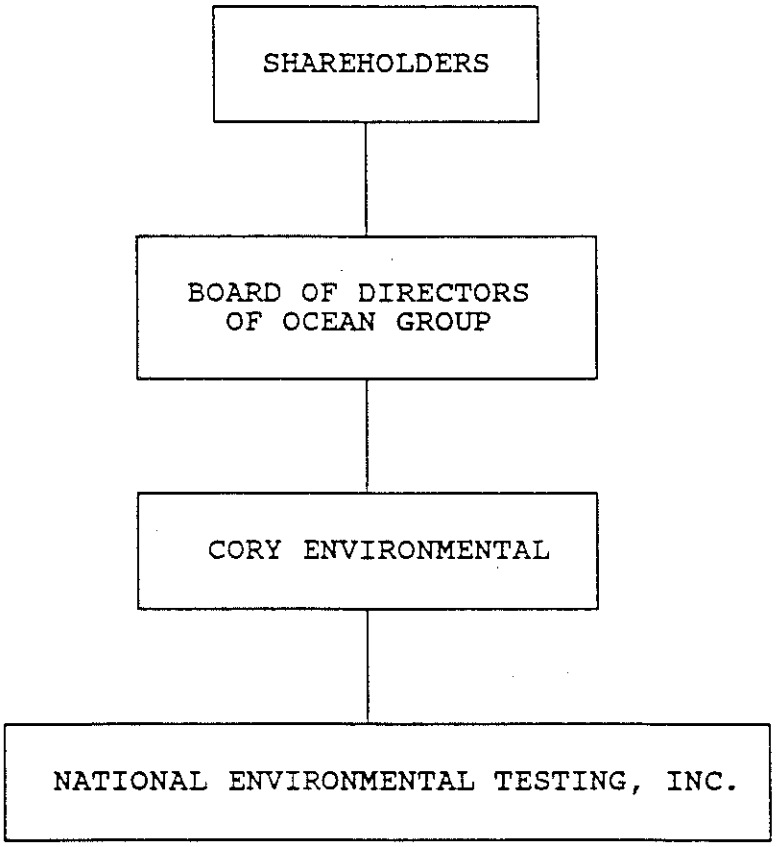
- Administer the NQAP so that the data produced by NET laboratories is of known and consistently high quality;
- Manage the ITP;
- Conduct systems audits of the Division Laboratories;
- Manage the Data Quality Audit Program;
- Make biannual written reports to the Corporate Officers and General Managers regarding the implementation of the National Quality Assurance Plan;
- Assist in writing and initiating NET Standard Operating Procedures (SOPs) and QA Plans (QAPs);

- Be the repository for all Division QAPs which must conform to the requirements of the NQAP;
- Assist in updating the NQAP as necessary;
- Be the repository of all external Performance Evaluation (PE) and audit results in which NET Divisions participate;
- Monitor certification and accreditation status and assist with certification activities.

The Vice President of Operations shall:

- Communicate management support of the NQAP to all levels of the organization.
- Ensure implementation of the programs and adherence to the policies described in the National Quality Assurance Plan.

Figure 4.1: Organization of National Environmental Testing, Inc.



NATIONAL ENVIRONMENTAL TESTING , INC
New Management Structure
Effective January 27, 1992

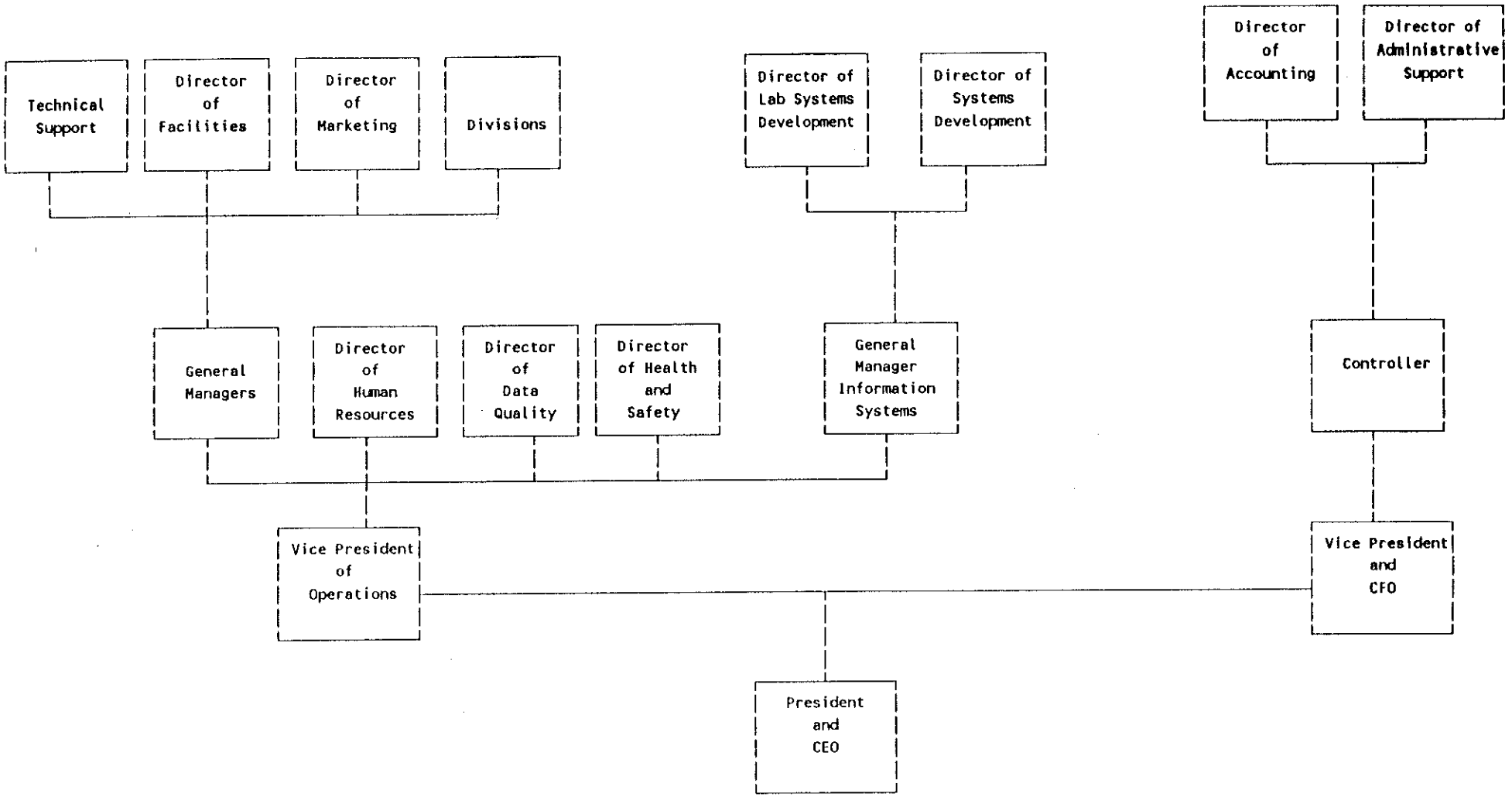


Figure 4.3 NET Quality Assurance Organizational Chart

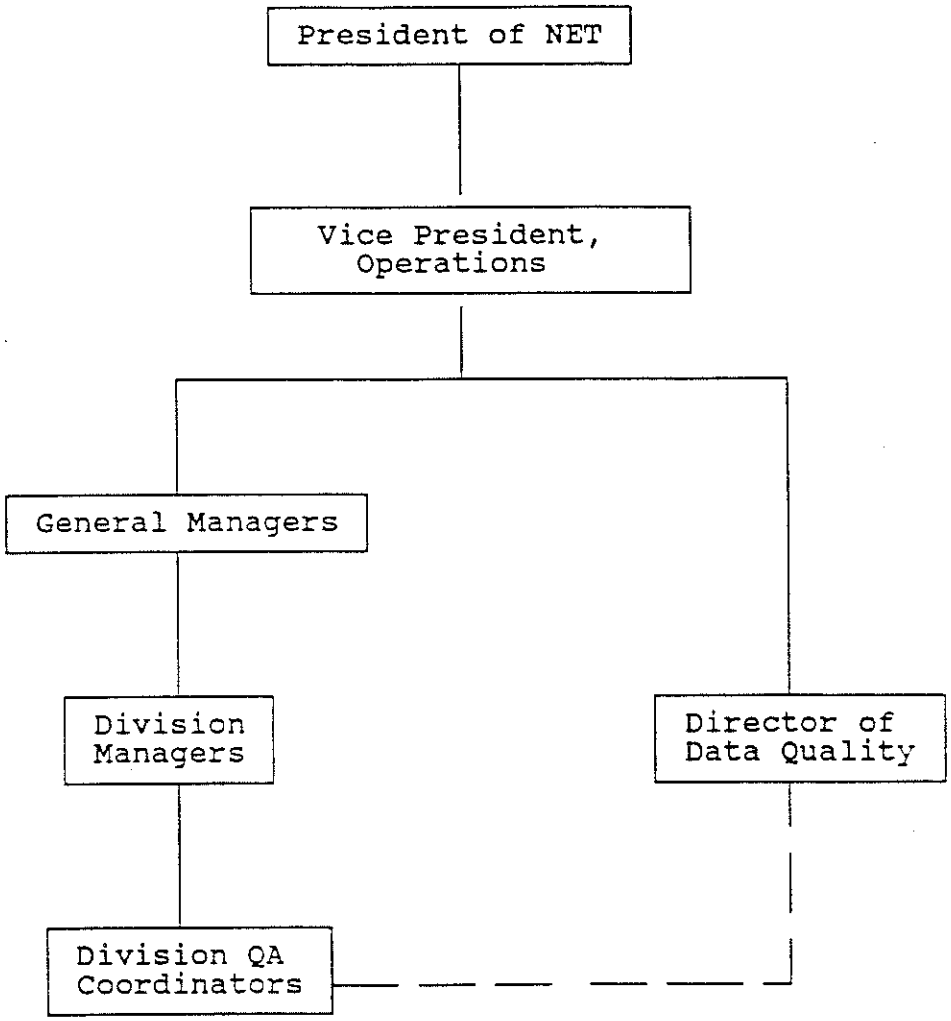
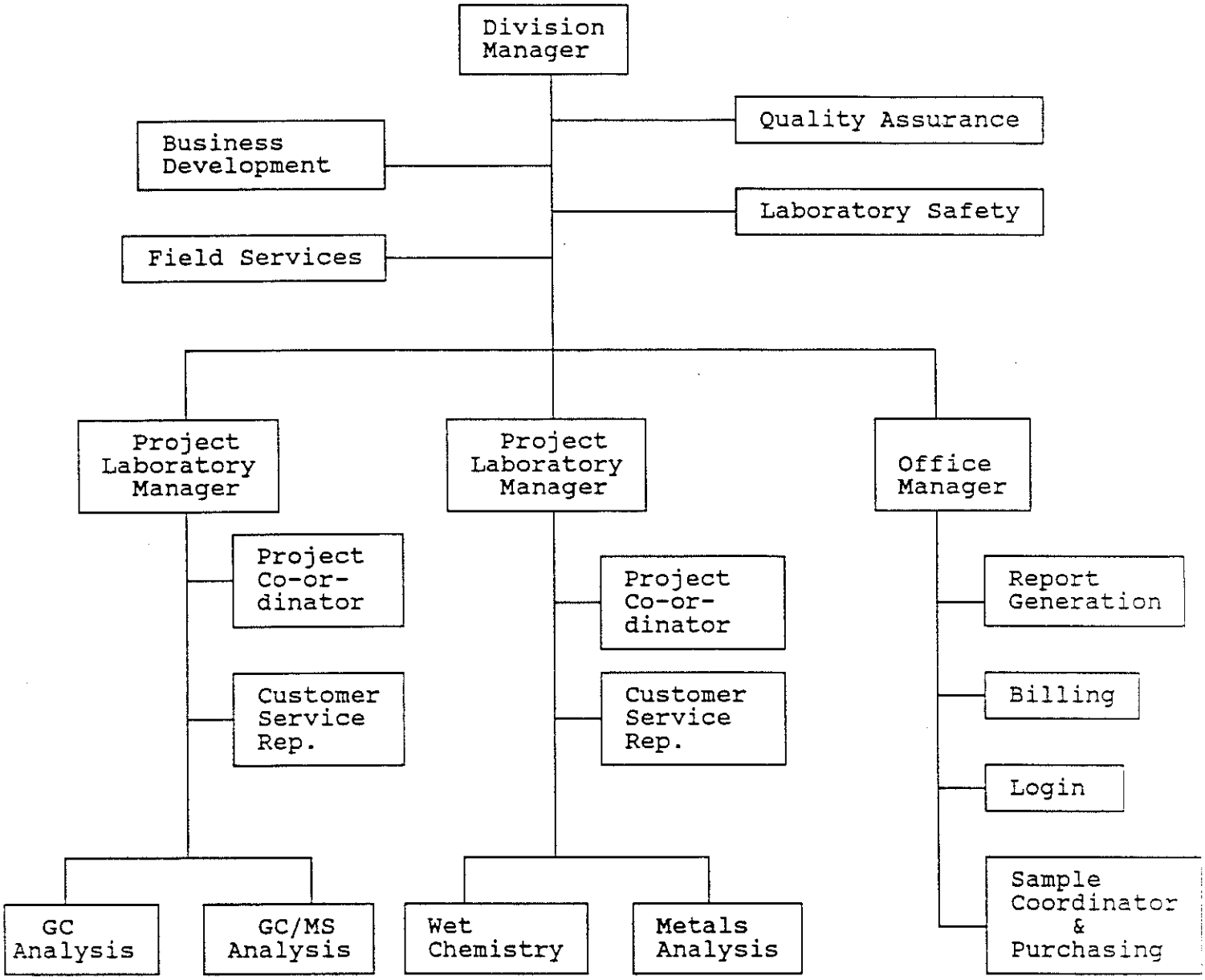


Figure 4.4 Organization of NET Inc. - Auburn Hills Division



SECTION 5

QA Objectives for Measurement Data

The Quality Assurance Objectives are to provide analytical data of known quality, to produce defensible analytical data and to produce data which meets the client's specific needs.

Data is assessed by precision, accuracy, representativeness and comparability. Data quality is also assessed by the analysis of Standard Reference Materials (SRMs) when available. In general, each method specifies the use and frequency of blank analysis, calibration standards, calibration check analyses, surrogate/matrix spikes and Standard Reference Materials to monitor method performance. The Quality Assurance Objectives for data quality of these quality control measures for the most commonly requested methods are summarized in Tables 5.1 through 5.11. The control limits listed are NET and EPA established.

As stated, the objectives of the Quality Assurance Program for the laboratory are to provide data of known quality. To accomplish this, NET-Auburn Hills will:

- Maintain an effective, ongoing QA/QC program that measures and verifies laboratory performance;
- Provide sufficient flexibility to allow controlled changes in routine methodology to meet project specific data requirements;
- Recognize as soon as possible and provide correction for any factors which adversely affect data quality;
- Monitor operational performance of the laboratory on a routine basis and provide corrective action as needed; and,
- Maintain complete records of sample submittal, raw data, laboratory performance, and complete analyses to support reported data.

Precision

Precision is a measure of the mutual agreement among individual measurements of the same parameter under similar conditions. Precision is usually expressed as relative percent difference and is evaluated through the use of matrix spike/matrix spike duplicates or through duplicate analysis when matrix spiking is not possible. A matrix is a portion of sample which has a known quantity of analyte added to it. Matrix spikes also help assess the effects of the matrix on the analyte.

Accuracy

Accuracy is a measure of the degree of agreement between an analytical value and the true or accepted reference value where it is known. Accuracy is usually expressed as percent recovery and is evaluated through the use of matrix spike/matrix spike duplicates and /or through laboratory control samples especially when matrix spiking is not possible.

Completeness

Completeness is a measure of the amount of valid data obtained from the analytical measurement system. It is defined as the total number of samples taken for which acceptable analytical data are generated, divided by the total number of samples collected, multiplied by 100. Every attempt will be made to generate completely valid data. However, it is recognized that some samples may be lost or invalidated in the laboratory and that some results may be deemed questionable based on internal QC results. The objective will be to have 90 percent completeness.

Representativeness

Representativeness is a measure of how closely the measured results reflect the actual concentration or distribution of the chemical compounds in the sample. For any project, sampling will be performed by the customer or the customer's contractors. Sample handling protocols (ie., storage, preservation and transportation) have been developed to preserve the representativeness of the collected samples. Proper documentation will establish that protocols have been followed and sample identification and integrity have been assured. Every attempt will be made to ensure that the aliquots taken for analyses are representative of the sample received.

Comparability

The generation of comparable data is the goal of any analytical program. This characteristic implies strict adherence to published analytical protocols and use of standard reporting units. NET's QA/QC program is structured to ensure adherence to the proper analytical protocols and to fully ensure documentation of these procedures. The QA objective is that all data resulting from these analyses be comparable with other measurements made by NET or another organization.

Table 5.1

Quality Assurance Objectives for Metals -
Atomic Absorption, Flame and Furnace

Quality Control Measure	Analyte	Control Limits
Calibration Curve (3 point curve)	All	Correlation Coefficient ≥ 0.9995
Initial Calibration Verification (ICV) (External Standard from an approved independent source)	All	Accuracy 90 - 110%
Reagent Blank	All	< Reporting Limit
Procedure Blank	All	< Reporting Limit
Continuing Calibration Verification (CCV) (Mid Standard)	All	Accuracy* 90 - 110%
Laboratory Control Standard (LCS)	All	Accuracy* 80 - 120%
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	All	Accuracy* 75 - 125% Precision ≤ 20% RPD**
Reporting Limit Verification Standard (RLVS)	All	Advisory Limits 75 - 125%

* Statistically determined control limits will be developed in the near future with accuracy being acceptable within +/- 3 standard deviations from the mean.

** RPD - Relative Percent Difference - Defined in Section 14.

Table 5.2

Quality Assurance Objectives for Metals -
Inductively Coupled Plasma

Quality Control Measures	Analyte	Control Limits
Calibration Curve (2 standard calibration or manufacturer's procedures)	All	Correlation Coefficient $\geq$ 0.995
Initial Calibration Verification (ICV) (External Standard from an approved source)	All	Accuracy 90 - 110%
Reagent Blank	All	< Reporting Limit
Procedure Blank	All	< Reporting Limit
Continuing Calibration Verification (CCV) (Mid Standard)	All	Accuracy* 90 - 110%
Laboratory Control Standard (LCS)	All	Accuracy* 80 - 120%
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	All	Accuracy* 75 - 125% Precision $\leq$ 20% RPD**

* Statistically determined control limits will be developed in the near future with accuracy being acceptable within +/- 3 standard deviations from the mean.

** RPD - Relative Percent Difference - defined in Section 14.

Table 5.3

Quality Assurance Objectives for Wet Chemistry Parameters

Quality Control Measure	Analyte	Control Limits
Calibration Curve (Referenced Curve: 5 standard calibration Daily Curve: 3 standard calibration)	All Possible	Correlation Coefficient $\geq$ 0.995
Initial Calibration Verification (ICV) (External standard from an approved source)	All Possible	Accuracy 90 - 110% (or the control limits we receive from the source)
Reagent Blank	All Possible	< Reporting Limit
Procedure Blank	All Possible	< Reporting Limit
Continuing Calibration Verification (CCV) (Mid Standard)	All Possible	Accuracy* 90 - 110%
Laboratory Control Standard (LCS)	All Possible	Accuracy* 80 - 120%
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	All Possible	Accuracy* 75 - 125% Precision $\leq$ 20% RPD**
Duplicate	Parameters that cannot be spiked	Precision $\leq$ 20% RPD**

* Statistically determined control limits will be developed in the near future with accuracy being acceptable within +/- 3 standard deviations from the mean.

** RPD - Relative Percent Difference - Defined in Section 14.

Table 5.4

Quality Assurance Objectives for GC/MS Volatiles
Methods 624/8240

Quality Control Measure	Analyte	Control Limits	
Procedure Blank	Reagent Grade Water All method analytes	< Reporting Limit	
Tune Check	Bromofluorobenzene	Must met specific ion method specifications	
Initial Calibration Verification (ICV)	Approximately 90% of calibrated compounds	Accuracy +/- 30% of the true value.	
Continuing Calibration Verification (CCV)	Calibration Check Compounds (CCC)	< 25% RPD of RF* from the initial calibration	
		Accuracy	
		Water	Other
Surrogate Standard Compounds	1,2-Dichloroethane-d4	76-114%	70-121%
	Toluene-d8	88-110%	81-117%
	Bromofluorobenzene	86-115%	74-121%
Matrix Spike(MS)	1,1-Dichloroethylene	61-145%	59-172%
	Trichloroethylene	71-120%	62-137%
	Benzene	76-127%	66-142%
	Toluene	76-125%	59-139%
	Chlorobenzene	75-130%	60-133%
		Precision	
		Water	Other
Matrix Spike Duplicate (MSD)	1,1-Dichloroethylene	≤ 14%	≤ 22%
	Trichloroethylene	≤ 14%	≤ 24%
	Benzene	≤ 11%	≤ 21%
	Toluene	≤ 13%	≤ 21%
	Chlorobenzene	≤ 13%	≤ 21%

* RF - Response Factor

Table 5.5

Quality Assurance Objectives for GC/MS Semi-Volatiles
Methods 625/8270

Quality Control Measure	Analyte	Control Limits	
Procedure Blank	All Method Analytes	< Reporting Limit	
Tune Check	Decafluorotriphenylphosphine	Must meet specific ion method specifications	
Initial Calibration Verfification (ICV)	Approximately 90% of Calibrated Compounds	Accuracy +/- 30% of the true value.	
Continuing Calibration Verification (CCV)	Calibration Check Compounds (CCC)	RF*< 30% from the initial calibration	
		Accuracy	
		Water	Other
Surrogate Standard Compounds	Nitrobenzene-d5	35-114%	23-120%
	2-Fluorobiphenyl	43-116%	30-115%
	p-Terphenyl	33-141%	18-137%
	Phenol-d6	10- 94%	24-113%
	2-Fluorophenol	21-110%	25-121%
	2,4,6-Tribromophenol	10-123%	19-122%
Matrix Spike (MS)	1,2,4-Trichlorobenzene	39- 98%	38-107%
	Acenaphthene	46-118%	31-137%
	2,4-Dinitrotoluene	24- 96%	28- 89%
	Pyrene	26-127%	35-142%
	n-Nitroso-di-n-propylamine	41-116%	41-126%
	1,4-Dichlorobenzene	36- 97%	28-104%
	Pentachlorophenol	9-103%	17-109%
	Phenol	12- 89%	26- 90%
	2-Chlorophenol	27-123%	25-102%
	4-Chloro-3-methylphenol	23- 97%	26-103%
	4-Nitrophenol	10- 80%	11-114%
		Precision	
Matrix Spike Duplicate (MSD)	1,2,4-Trichlorobenzene	≤ 28%	≤ 23%
	Acenaphthene	≤ 31%	≤ 19%
	2,4-Dinitrotoluene	≤ 38%	≤ 47%
	Pyrene	≤ 31%	≤ 36%
	n-Nitroso-di-n-propylamine	≤ 38%	≤ 38%
	1,4-Dichlorobenzene	≤ 28%	≤ 27%
	Pentachlorophenol	≤ 50%	≤ 47%
	Phenol	≤ 42%	≤ 35%
	2-Chlorophenol	≤ 40%	≤ 50%
	4-Chloro-3-methylphenol	≤ 42%	≤ 33%
	4-Nitrophenol	≤ 50%	≤ 50%

* RF - Response Factor

Table 5.6

Quality Assurance Objectives for GC Pesticides and PCBs
Method 608/8080

Quality Control Measure	Analyte	Control Limits
Procedure Blank	All	< Reporting Limit
Degradation Check	Endrin	< 20% breakdown
Inital Calibration Verification (ICV)	All	Accuracy 60 - 130%
Continuing Calibartion Verification (CCV)	All	Accuracy 60 - 130%
Surrogate Standard Compound	2,4,5,6-Tetra-chloro-m-xylene	Accuracy 24 - 150%
		Accuracy*
Laboratory Control Standard (LCS)	Aldrin	60 - 120 %
	a-BHC	60 - 120 %
	b-BHC	50 - 125 %
	g-BHC	60 - 120 %
	d-BHC	60 - 120 %
	Chlordane	60 - 120 %
	4,4' -DDD	60 - 120 %
	4,4' -DDE	60 - 120 %
	4,4' -DDT	60 - 120 %
	Dieldrin	60 - 120 %
	Endosulfan I	60 - 120 %
	Endosulfan Sulfate	55 - 120 %
	Endrin	60 - 120 %
	Heptachlor	60 - 120 %
	Heptachlor Epoxide	60 - 120 %
	Toxaphene	60 - 120 %
	Endrin Aldehyde	Mean +/- 3 Std Dev*
	Methoxychlor	Mean +/- 3 Std Dev*
	Aroclor 1016	60 - 120 %
	Aroclor 1221	60 - 120 %
	Aroclor 1232	60 - 120 %
	Aroclor 1242	60 - 120 %
	Aroclor 1248	60 - 120 %
	Aroclor 1254	60 - 120 %
	Aroclor 1260	60 - 120 %

* To be determined by Statistical Process Control.

Table 5.6 Cont.

Quality Assurance Objectives for GC Pesticides and PCBs
Method 608/8080

Quality Control Measure	Analyte	Control Limits
		Accuracy
Matrix Spike (MS)	Aldrin	50 - 130 %
	a-BHC	50 - 130 %
	b-BHC	40 - 130 %
	g-BHC	50 - 130 %
	d-BHC	50 - 130 %
	Chlordane	50 - 130 %
	4,4' -DDD	50 - 130 %
	4,4' -DDE	50 - 130 %
	4,4' -DDT	50 - 130 %
	Dieldrin	50 - 130 %
	Endosulfan I	50 - 130 %
	Endosulfan Sulfate	45 - 130 %
	Endrin	50 - 130 %
	Heptachlor	50 - 130 %
	Heptachlor Epoxide	50 - 130 %
	Toxaphene	50 - 130 %
	Endrin Aldehyde	Mean +/- 3 Std Dev*
	Methoxychlor	Mean +/- 3 Std Dev*
	Aroclor 1016	50 - 130 %
	Aroclor 1221	50 - 130 %
	Aroclor 1232	50 - 130 %
	Aroclor 1242	50 - 130 %
	Aroclor 1248	50 - 130 %
	Aroclor 1254	50 - 130 %
	Aroclor 1260	50 - 130 %
Matrix Spike Duplicate (MSD)	All	Precision** ≤ 25%

* To be determined by Statistical Process Control.

** RPD - Relative Percent Difference - Defined in Section 14.

Table 5.7

Quality Assurance Objectives for Volatile Organics
Methods 601/8010

Quality Control Measure	Analyte	Control Limits
Procedure Blank	All	< Reporting Limits
		Accuracy*
Initial Calibration Verification (ICV)	Methylene Chloride	85 - 115%
	1,1-Dichloroethane	85 - 115%
	Chloroform	85 - 115%
	1,1,1-Trichloroethane	85 - 115%
	Trichloroethylene	85 - 115%
	Tetrachloroethylene	85 - 115%
		Accuracy*
Continuing Calibration Verification (ICV)	Methylene Chloride	80 - 120%
	1,1-Dichloroethane	80 - 120%
	Chloroform	80 - 120%
	1,1,1-Trichloroethane	80 - 120%
	Trichloroethylene	80 - 120%
	Tetrachloroethylene	80 - 120%
Surrogate Standard Compound	Chlorobutane	80 - 120%
		Accuracy*
Matrix Spike (MS)	Methylene Chloride	60 - 135%
	1,1-Dichloroethane	70 - 120%
	Chloroform	70 - 130%
	1,1,1-Trichloroethane	60 - 125%
	Trichloroethylene	50 - 135%
	Tetrachloroethylene	65 - 125%
		Precision**
Matrix Spike Duplicate (MSD)	Methylene Chloride	≤ 25%
	1,1-Dichloroethane	≤ 25%
	Chloroform	≤ 25%
	1,1,1-Trichloroethane	≤ 25%
	Trichloroethylene	≤ 25%
	Tetrachloroethylene	≤ 25%

* To be determined by Statistical Process Control
** RPD - Relative Percent Difference - Defined in Section 14.

Table 5.8

Quality Assurance Objectives for Volatile Organic Compounds
Methods 602/8020

Quality Control Measures	Analyte	Control Limits
Procedure Blank	All	< Reporting Limit
		Accuracy
Initial Calibration Verification (ICV) Calibration	Benzene	85 - 115%
	Ethyl Benzene	85 - 115%
	Toluene	85 - 115%
	Xylene	85 - 115%
		Accuracy*
Continuing Calibration Verification (CCV)	Benzene	80 - 120%
	Ethyl Benzene	80 - 120%
	Toluene	80 - 120%
	Xylene	80 - 120%
Surrogate Standard Compound	n-Propylbenzene	80 - 120%
		Accuracy*
Matrix Spike (MS)	Benzene	50 - 150%
	Toluene	60 - 135%
	Ethyl Benzene	60 - 125%
	Xylene	60 - 125%
Matrix Spike Duplicate (MSD)		Precision**
	Benzene	≤ 25%
	Toluene	≤ 25%
	Ethyl Benzene	≤ 25%
	Xylene	≤ 25%

* To be determined by Statistical Process Control.

** RPD - Relative Percent Difference - Defined in section 14.

Table 5.9

Quality Assurance Objectives for PNA
Method 610/8310

Quality Control Measure	Analyte	Control Limits
Procedure Blank	All	< Reporting Limit
Inital Calibration Verification (ICV)	All	Accuracy 80 - 120%
Continuing Calibration Verficiation (CCV)	All	Accuracy 80 - 120%
Surrogate Standard Compund	2-Flurobiphenyl	Accuracy 40 - 140%
		Accuracy*
Laboratory Control Standard (LCS)	Naphthalene	55 - 120 %
	Acenaphthylene	45 - 125 %
	Anthracene	50 - 120 %
	Fluoranthene	50 - 120 %
	Pyrene	45 - 125 %
	Benzo(b)fluoranthene	50 - 120 %
	Benzo(a)pyrene	45 - 125 %
	Indeno(1,2,3-cd)perylene	45 - 125 %
		Accuracy*
Matrix Spike (MS)	Naphthalene	50 - 125%
	Acenaphthylene	45 - 125%
	Anthracene	45 - 125%
	Fluoranthene	45 - 125%
	Pyrene	45 - 125%
	Benzo(b)fluoranthene	45 - 125%
	Benzo(a)pyrene	40 - 125%
	Indeno(1,2,3-cd)perylene	40 - 125%
Matrix Spike Duplicate (MSD)	All	Precision** ≤ 25%

* To be determined by Statistical Process Control.
** RPD - Relative Percent Difference - Defined in Section 14.

Table 5.10

Quality Assurance Objectives for Herbicides
Methods 615/8150

Quality Control Measures	Analyte	Control Limits
Method Blank	All	< Reporting Limit
		Accuracy
Initial Calibration Verification (ICV)	2,4-D	85 - 115%
	2,4,5-TP	85 - 115%
		Accuracy*
Continuing Calibration Verification (CCV)	2,4-D	80 - 120%
	2,4,5-TP	80 - 120%
		Accuracy*
Laboratory Control Standard (LCS)	2,4-D	60 - 130%
	2,4,5-TP	60 - 130%
		Accuracy*
Matrix Spike (MS)	2,4-D	50 - 130%
	2,4,5-TP	50 - 130%
		Precision**
Matrix Spike Duplicate (MSD)	2,4-D	≤ 25%
	2,4,5-TP	≤ 25%

* To be determined by Statistical Process Control.
** RPD - Relative Percent Difference - defined in Section 14.

Table 5.11

Quality Assurance Objectives for the determination of Coliforms

Quality Control Measures	Analyte	Control Limit
Monthly Blank	Fecal Coliforms	< 1 Colony
	Total Coliforms	< 1 Colony
Monthly Standard	Fecal Coliforms	Source supplied
	Total Coliforms	Source supplied

SECTION 6

Sampling Procedures

A critical aspect which can affect the final conclusions made from a sample is the sample collection process. To assure the reliability of the sample data, quality control measures are included in field sample collection. Result validity is aided by required equipment maintenance and calibration, sampling, transportation, preservation identification of samples and chain-of-custody procedures.

Guidelines for a particular project are based upon site specific requirements. Field sampling personnel rely on Standard Operating Procedures (SOPs) for sampling client specified sampling location(s). The field sampling SOP details the collection, maintenance and specific calibration procedures for sampling equipment.

Selection on the type of sampling procedure to be used is project dependent. Sampling conducted to conform to client needs accounts for the type of analysis being requested and meeting EPA guidelines. Background information is gathered to determine the scope of sampling requirements and identify any potential safety risks. Information must be collected and documented as to the types of hazards that may be present during collection.

The material from which sampling equipment is constructed can affect analytical results. The material selected for sampling certain parameters must not contaminate or alter the sample being collected, and must be easily cleaned or disposed of so that samples are not cross-contaminated. Field personnel select equipment based upon the sample matrix and parameters being sampled.

NET - Auburn Hills recognizes that proper containers and appropriate preservatives are necessary for the collection of valid samples. In addition, the samples must be analyzed within parameter specific holding times. The Sample Preservative Summary (Table 6.1) details recommended sample containers, preservatives, holding times and the volume of sample needed.

During the training period for new personnel, the employee receives instructions on: sample site selection, selection and preparation of equipment and materials, sample collection for various media, preservation, documentation, and sample handling.

Personnel attend an Occupational Safety and Health Administration (OSHA) approved 40 hour Safety Training Workshop. Also Auburn Hills' OSHA approved Hazard Communication Program for field services includes client specific safety information where appropriate. Confined Space Entry training is received in conformance with all applicable OSHA requirements.

Table 6.1

Sample Preservation Summary

Parameter	Container [G=Glass] [P=Plastic]	Preservation	Recommended Holding Time	Minimum Volume
WET CHEMISTRY				
Alkalinity	P,G	4°C	14 days	100 ml
API Gravity	P,G	4°C	none	250 ml
Asbestos	P,G	4°C	none	1 L
Ash	P,G	4°C	none	10 gm
Biochemical Oxygen Demand (BOD)	P,G	4°C	48 Hours	1 L
Bottom Sediment & Water (BSW)	P,G	4°C	none	100 ml
British Thermal Units (BTU)	P,G	4°C	none	5 gm
Bromide	P,G	4°C	28 days	200 ml
Chemical Oxygen Demand (COD)	P,G	4°C H_2SO_4	28 days	50 ml
Chloride	P,G	none	28 days	200 ml
Chlorine, Total Residual	P,G	4°C	Immediately	100 ml
Chlorine Demand	G	4°C	Immediately	200 ml
Chloramines	G	4°C	Immediately	1 L
Coliform, Fecal	P (sterile)	4°C $Na_2S_2O_3$	6 hours	150 ml
Coliform, Total	P (sterile)	4°C $Na_2S_2O_3$	6 hours	150 ml

Table 6.1 (Con't)

Parameter	Container [G=Glass] [P=Plastic]	Preservative	Recommended Holding Time	Minimum Volume
E. Coli	P (sterile)	4°C $Na_2S_2O_3$	6 hours	150 ml
Color	P,G	4°C	48 hours	100 ml
Conductivty, Specific	P,G	4°C	28 days	100 ml
Cyanide, Amenable	P,G	4°C NaOH	14 days	1 L
Cyanide, Total	P,G	4°C NaOH	14 days	1 L
Density	G	4°C	28 days	1 L
Fluoride	P,G	4°C	28 days	300 ml
Flashpoint	P,G	4°C	none	100 ml
Hardness	P,G	4°C	28 days	200 ml
Hydrogen Ion, pH	P,G	none	Immediately	50 ml
Nitrogen, Ammonia	P,G	4°C H_2SO_4	28 days	400 ml
Nitrogen, Kjeldahl	P,G	4°C H_2SO_4	28 days	500 ml
Nitrogen, Nitrate	P,G	4°C	48 hours	100 ml
Nitrogen, Nitrite	P,G	4°C	48 hours	50 ml
Odor	P,G	4°C	24 hours	200 ml
Oil & Grease	G	4°C H_2SO_4	28 days	1 L
Dissolved Oxygen	P,G	none	Immediately	300 ml

Table 6.1 (Con't)

Parameter	Container [G=Glass] [P=Plastic]	Preservative	Recommended Holding Time	Minimum Volume
Paint Filter Test	P,G	4°C	none	100 ml
Phenolics	G	4°C H_2SO_4	28 days	1 L
Phosphorus, Ortho	P,G	4°C H_2SO_4	48 hours	50 ml
Phosphorus, Total	P,G	4°C H_2SO_4	28 days	50 ml
Reactivity, Statement	G	4°C	none	10 gm
Silica	P,G	4°C	28 days	50 ml
Solids, Total	P,G	4°C	7 days	100 ml
Solids, Dissolved	P,G	4°C	7 days	100 ml
Solids, Suspended	P,G	4°C	7 days	100 ml
Solids, Volatile	P,G	4°C	7 days	100 ml
Solids, Settable	P,G	4°C	48 hours	100 ml
Sulfate	P,G	4°C	28 days	50 ml
Sulfide	P,G	4°C Zinc Acetate NaOH	7 days	500 ml
Sulfite	G	4°C	Immediately	100 ml
Surfactants (MBAS)	P,G	4°C	48 hours	400 ml
Sulfur	P,G	4°C	none	10 gm
Total Petroleum Hydrocarbons (soil)	G	4°C	none	50 gm
(water)	G	4°C	H_2SO_4	1 L
Total Organic Carbon	P,G	4°C	28 days	50 ml
Total Organic Halogens		4°C Zero Headspace	28 days	100 ml

Table 6.1 (Con't)

Parameter	Container [G=Glass] [P=Plastic]	Preservative	Recommended Holding Time	Minimum Volume
Toxicity				
EP Toxicity	G	4°C	7 days	100 gm
TCLP	G	4°C	14 days	100 gm
Oil Waste Extraction	G	4°C	7 days	100 gm
Turbidity	P,G	4°C	48 hours	100 ml
Water Content	G	4°C	none	10 gm
METALS				
Chromium, Hexavalent	P,G	4°C	24 hours	100 ml
Mercury	P,G	4°C HNO_3	28 days	100 ml
Metals, except above	P,G	4°C HNO_3	6 months	1 L
ORGANICS				
Volatiles	G	4°C Zero Headspace HCL	14 days	100 ml (3 - 40 ml vials)
Pesticides/PCB's	G	4°C	7 days prior to extraction 40 days after extraction	4 L
Michigan Critical Materials	G	4°C	7 days Prior to extraction 40 days after extraction	4 L

* For TCLP Extraction only.

Table 6.1 (Con't)

Parameter	Container [G=Glass] [P=Plastic]	Preservative	Recommended Holding Time	Minimum Volume
Priority Pollutants	G	4°C	7 days prior to extraction 40 days after extraction	4 L
Herbicides	G	4°C	7 days prior to extraction 40 days after extraction	4 L
Semivolatile Organics Acid/Base/Neutral Extractables	G	4°C	7 days prior to extraction 40 days after extraction	4 L
Polynuclear Aromatic Hydrocarbons	G	4°C	7 days prior to extraction 40 days after extraction	4 L
Phenols	G	4°C	7 days prior to extraction 40 days after extraction	4 L
Phthalate Esters	G	4°C	7 days prior to extraction 40 days after extraction	4 L

SECTION 7

Sample Custody

Introduction

Laboratory analyses are performed to produce data representative of the conditions under which the sample was obtained. To provide representative samples for analysis, both field and laboratory personnel must perform their activities well.

Chain-of-Custody Procedure

The chain-of-custody is the record of sample handling from the time of sample collection to storage after analysis. The chain-of-custody is a detailed record of the sample description, collection information (ie., sampling location, date, time) required analysis list, and transfer of custody from sample collection through sample receipt into the laboratory.

When samples arrive at NET-Auburn Hills, the login personnel document any observed problems with the shipping containers, sample identification discrepancies and sample analysis discrepancies on the sample disposition form. The sample disposition form documents problems or discrepancies associated with a sample (See Figure 7.7). Sample label information is checked against the custody record and the condition of the sample noted. Samples are then logged into the laboratory data system which assigns a unique lab sample number. When sample login is complete, the system generates a bottle label which includes the unique lab number, the client identification, the sample description, and the date of collection. Lab sample labels are affixed to corresponding bottles and compared to the bottle ID for verification.

Once the sample login is complete, the sample custodian is responsible for proper placement of samples within the laboratory. Samples will be stored under appropriate conditions prior to preparation and analysis. Sample access is limited to NET-Auburn Hills personnel. Furthermore, security of the laboratory is maintained by an electronic alarm system. In the instance where a sample is transferred to an outside laboratory, sample identification records are verified against the sample label and transfer documents maintained.

Sample Field Collection and Shipping

The sample collection person must first consider the analyses to be performed so that proper sample containers can be obtained. When NET Auburn Hills field personnel are collecting the samples, field notes are compiled. All records required for documentation of sample collection by NET field personnel must be completed by the field personnel. The primary documenting record for the field personnel is the field note. Figures 7.1 to 7.5 illustrate the various field note documents used for particular types of sample collection. After completing the field note, the field personnel must review all sample labels for correct information and preservation.

If samples are collected by the client a chain-of-custody form must be completed. Figure 7.6 represents the NET Auburn Hills chain-of-custody form which is the primary documenting record for the sample when someone other than NET Auburn Hills field personnel have collected the sample.

Samples must be placed in containers compatible with the intended analysis and must be preserved properly. Also, sample collection must allow for the time interval between acquiring the sample and analysis (holding time) so that the sample is representative. Table 6.1 provides requirements for various analytical parameters with respect to the type of containers,preservation methods, and maximum holding times between collection and analysis.

Polyethylene or glass containers are required and, in most cases, samples must be cooled to 4°C.

The chain-of-custody/field note record shall be signed by each individual who has the sample in his/her possession:

- The chain-of-custody record shall be initiated in the field by the person collecting the sample, for every sample;

- If the person collecting the sample does not transport the samples to the laboratory or the sample containers for shipment, the first block for "Relinquished By, Received By" shall be signed by the field personnel;

- The person transporting the samples to the laboratory by delivering them for shipment shall sign the record form as "Relinquished By";

- If the samples are shipped to the laboratory by commercial carrier, the chain-of-custody form shall be sealed in a watertight container, and the shipping containers shall be sealed before they are given to the carrier.

- If the samples are shipped by commercial carrier, the waybill shall serve as an extension of the chain-of-custody record between the final field custodian and the laboratory.

- If the samples are transported directly to the laboratory, the chain-of-custody shall be kept in possession of the person delivering the samples.

- Upon receipt in the laboratory, the login personnel shall open the shipping containers, compare the contents with the chain-of-custody record, and sign, date, and make note of any discrepancies on the chain-of-custody form.

- If discrepancies occur, the samples in question shall be segregated from the normal sample storage and appropriate notification made immediately. A sample disposition form is completed with all discrepancies clearly noted.

- The chain-of-custody records shall be maintained with the records for a specific project, becoming part of the project file.

- If a client requests a change to be made on the chain of custody (ie., analysis requested) once the samples are in NET-Auburn Hills possession, the item to be changed will have a single line put through it and the new item added. All changes are initialed and dated by the person making the change. Also a sample disposition form is attached with explanations as to why the change occurred.

Multipart chain-of-custody forms may be used so that one copy can be returned to the person shipping the samples after receipt in the laboratory.

Laboratory Document Control

The goal of the document control program is to assure that all documents for a group of samples will be accounted for when the project is completed. All observations and results recorded by NET Auburn Hills are entered into pre-printed data sheets or into permanent laboratory notebooks. Data records are referenced with the sample, date, batch number and analyst's initials.

All documentation in notebooks and other documents shall be in ink. If an error is made in a notebook a single line is placed through the error and the correct information is entered next to the error. All errors/corrections are initialed and dated.

Laboratory Storage of Samples

The primary considerations for sample storage are:

- Maintaining prescribed temperature which, if required, typically is 4°C; and,

- Extracting and/or analyzing samples within the prescribed holding times for the parameters of interest.

The temperature and holding time requirements of Table 6.1 shall be used. Placing samples in the proper storage environment is the responsibility of each analyst. Should a sample need immediate attention due to a holding time or collection problem, the login personnel will notify either the Customer Service Representative or the Project Manager for assistance.

Sample Disposal

Several possibilities for sample disposal exist:

- The sample may be consumed completely during analysis;

- Sample may be returned to the customer or location of sampling for disposal; or,

- The sample may be stored after analysis. (Samples are normally maintained no longer than two months from receipt unless otherwise requested).

Proper environmental control and holding times must be observed if re-analysis is anticipated. If re-analysis is not anticipated, environmental conditions for storage need not be observed.

The Project Manager shall determine disposal of samples if not specified on the chain-of-custody.

Figure 7.1 Field Notes: Pick-Up Form

FIELD NOTES
PICK-UPS AND DROP-OFFS

Date Completed_____

Personnel_____

Date	Time	Location	P/U	D/O	Observers

Comments:

Chain-of-Custody: Relinquished by: _____ Date: _____

Received by: _____ Date: _____

Figure 7.2 Field Notes: Grab Sampling

GRAB SAMPLING
FIELD NOTES AND OBSERVATIONS

Account: _____ Date: _____

Field Personnel: _____ Observers: _____

Weather: _____ Time on Site: _____

Sample ID	Type & Description of Containment	Sampling Method	Sample Bottle	Sample Description

Comments:

Chain-of-Custody: Relinquished by: _____ Date: _____

Received by: _____ Date: _____

Figure 7.3 Field Notes: 24 Hour Composites

Date Completed: _____

FIELD NOTES & OBSERVATIONS

Account: _____ Field Personnel: _____

Site ID: _____ Field Sample No. _____ Observers: _____

Composite Sample Data: Timed Interval: _____ Proportional: _____

Sampling Initiated: Time: _____ Date: _____ Weather: _____

Sampling Completed: Time: _____ Date: _____ Weather: _____

Grab Sample Data: Direct: _____ Other: _____

Sampling Collected: Time: _____ Date: _____ Weather: _____

Flow Measurement: Instantaneous: _____; 24-HR. Measurement: _____

Comments for Report:

_____

Raw Flow Data:

Instantaneous: Time: _____ Date: _____ Weather: _____

Pipe Diameter: _____ Primary Device: _____ HD.HT: _____ Vel: _____

Actual Measurement: Primary Device _____ HD. HT. At Set-Up: _____

Set-Up: Time: _____ Date: _____ Weather: _____

Take-Down: Time: _____ Date: _____ Weather: _____

Totalizer Value: Initial: _____ Final: _____

SAMPLE BOTTLES COLLECTED:

	Grab	Comp		Grab	Comp		Grab	Comp	On Site Data:
F.S. Plain			VOA			CN			Chlorine Check: P.
Qt. Plain			TOX			Phenol			Sulfide Check: P.
Pt. Plain			1/2 Gal. Org.			Sulfide			pH _____
120 Plain			F.S. Back-up			Sterile Bottle			Temp (^{o}F) _____
Qt. HNO_3			F.S. H_2SO_4			Hypochlorite			Tot. Res. Cl _____
Pt. HNO_3			Pt. H_2SO_4			Dissolved O_2			Sulfite _____
120 HNO_3			120 H_2SO_4						Free Cl _____

Program: _____

In-House Comments:

Chain-of-Custody: Relinquished by: _____ Date: _____

Received by: _____ Date: _____

Figure 7.4 Field Notes: Monitoring Well data Sheet

Account: _____

Field Personnel: _____ Observers: _____

Date: _____ Weather: _____ Time on-site: _____

Date: _____ Weather: _____ Time on-site: _____

Well ID	Well Type	Static H2O Level (ft)	Bottom Depth (ft)	Date Evacuated	Method of Evacuation	Quantity Evacuated	3X (gal) Volume

Program: _____

Comments:

Figure 7.5 Field Notes: Groundwater Sample Collection

Account: _____

Date: _____ Time: _____ Weather: _____

Field Personnel: _____

Observers: _____

Well Identification: _____

Sampling Method: _____

Sample Appearance: _____

Total number of containers filled: _____ (list)

Filtered: _____

Non-Filtered: _____

pH - 1) _____ Conductivity - 1) _____

2) _____ 2) _____

3) _____ 3) _____

4) _____ 4) _____

Ge Dox - 1) _____ Temperature (degrees F) _____

2) _____

3) _____

4) _____

Comments: _____

_____

_____

WELL LOCK INFORMATION

Does the well have a lock? _____

General Condition: _____

Well locked upon completion: _____

Chain of Custody: Relinquished By: _____ Date: _____

Received By: _____ Date: _____

Figure 7.6 Chain-of-Custody Form

CHAIN OF CUSTODY

Client	Project Name
Send Report to:	
Address Telephone #	Collected by:

Invoice to: QC: yes no

Collection Information								Parameters									
Sample ID	Sample Location	Date	Time	GRAB	COMP	Sample Type	No. of Container										

Remarks: _____

_____

Relinquished by:	Date	Time	Received by:	Date	Time
Shipping Notes/Lab Comments			Received for NET by:		

Samples Field Filtered: ____Yes ____No
Seals intact upon receipt: ____Yes ____No ____N/A

Figure 7.7 SAMPLE DISPOSITION AND FOLLOW UP FORM

Client Name/Location: _____ Date: _____

Contact Person: _____

Phone Number: _____

Date Received: _____

NET Number(s): _____

Client I.D.: _____

_____

Statement of Problems:

( ) Chain of Custody missing/not filled out properly
( ) Damaged Container(s)
( ) Missing Container(s)
( ) Inadequate Sample Volume
( ) Inappropriate Container(s)/Preservatives
( ) Sample(s) do not match Client Program/Sales Order
( ) Sample Identification Unclear
( ) Missing Information/Paperwork
( ) Other (please describe): _____

_____

_____

_____

What is required to remedy problem? _____

_____

Internal Sales Coordinator Use:

Date: _____ Initials: _____ Contact Person: _____

Resolution/Disposition of Sample: _____

_____

_____

_____

-ATTACH TO LAB OFFICE COPY OF SAMPLE WORK ORDER-

SECTION 8

Calibration Procedures and Frequency

This section describes the calibration procedures used for the majority of the instrumentation in the laboratory as well as the frequency of such calibrations.

All materials used for instrument calibration will be of the highest purity available from a commercial source or from the U.S. Environmental Protection Agency Pesticide and Industrial Chemicals Repository or the National Bureau of standards.

GAS CHROMATOGRAPHY/MASS SPECTROSCOPY (GC/MS)

Calibration Standards

Stock solutions are high purity standards. The supplier, date prepared, expiration date, preparation procedure and the analyst who prepared the standard are documented in the standard preparation record book. All stock solutions are recorded in the standards preparation record book and given a unique identification number. From the stock, working standards are prepared by diluting the stock. The process is as follows:

1. Prepare stock solutions if necessary.
   Stock solutions for 8240/624 have a shelf life of two months. A typical replacement rate for these stock solutions is approximately every two weeks.

2. Prepare working standards by dilution of the stock standards or purchased ampules when appropriate. The shelf life of the ampules are the stated expiration date on the ampules.

3. Verify the working standards by analysis of an inital calibration verification standard using either U.S. EPA QC concentrates or other independent standards.

Calibration Procedures

An inital 5 point calibration curve is performed on each GC/MS instrument using calibration standards prepared as described above. Following the initial calibration the curve is monitored by the following quality control measures.

At the beginning of each shift that volatile organic analyses are performed using Methods 624/8240, the GC/MS system must be checked to verify that acceptable performance criteria are obtained for Bromofluorobenzene (BFB). The performance test must

be passed before analysis of samples, blanks or standards can begin. If the tune requirements cannot be met system maintenance may be necessary followed by a new 5 point calibration of the instrument.

At the beginning of each shift that semivolatile organic analyses are performed using Methods 625/8270, the GC/MS system must be checked to see if acceptable performance criteria are achieved for Decafluorotriphenylphosphine (DFTPP). The performance criteria must be achieved before analysis of sample, blanks, or standards are analyzed. If the tune requirements cannot be met system maintenance may be necessary followed by a new 5 point calibration of the instrument.

If tune acceptance criteria are met, a continuing calibration check standard (CCC) is analyzed next. The method specific CCC acceptance criteria must be met before analysis of samples can begin. For methods 624, 8240, 625 and 8270 System Performance Check Compounds (SPCC) are also analyzed and must meet acceptance criteria. If the CCC or SPCC criteria cannot be met then system maintenance may be required followed by a new calibration of the instrument.

All initial calibration data as well as the subsequent calibration verification data are documented.

GAS CHROMATOGRAPHY

Calibration Standards

Stock solutions are prepared from high purity standards. The supplier, date prepared, expiration date, preparation procedure and the analyst who prepared the standard are documented in the standard preparation record book. All stock solutions are recorded in the standard preparation record book and given a unique identification number. From the stock, working standards are prepared by diluting the stock.

Calibration Procedure

The instruments are calibrated using a minimum of 5 standards. The peak height/peak area versus the standard concentration is plotted to obtain the calibration curve.

The instruments are calibrated to maintain the acceptable continuing calibration verification standard recoveries. Instruments are also calibrated after any major system change such as the replacement of a column.

An initial calibration verification standard is analyzed with each new calibration. This standard is prepared from an independent source standard different than that used for the instrument calibration.

All initial and subsequent continuing calibration verifications are recorded.

INDUCTIVELY COUPLED PLASMA SPECTROSCOPY (ICP)
GRAPHITE FURNACE (GFAA)
FLAME (AA)

Calibration Standards

The calibration stock solutions and the calibration standards are prepared from NBS traceable standards. The lot number, supplier date prepared, date of expiration and the analyst who prepared the standard are recorded in the standard preparation record book. The process is as follows:

1. Calibration standards are prepared by dilution of the stock standard, usually 1000 ppm NBS traceable standards.

2. The calibration standards are prepared using the same type of acid or combination of acids as the sample will have after digestion, ie. matrix matched.

3. Calibration standards - Stock, Intermediate and Working Standard shelf life.

   1000 ppm Standards
   1 Year from date of opening

   Stock Standards

Furnace	3 Months

   Working Standards

Furnace	2 Months
Cold Vapor	Daily
ICP	Daily

Calibration Procedure

The instruments are calibrated for every analytical run sequence beginning with a blank and then three standards, analyzing them from lowest to the highest concentration. After the instrument is calibrated, the calibration curve is verified by analyzing an initial calibration verification sample (ICV). The calibration curve acceptance criteria is a correlation coefficient of >=0.9995. The ICV is an EPA quality control concentrate or an independent known from a supplier different than the supplier of the stock standard and it has a concentration that was not used to generate the curve.

If the ICV sample analysis exceeds the control limits or if the correlation coefficient is not met, the analysis is ended and the problem is investigated and corrected. The instrument is then recalibrated and the ICV analyzed again. Sample analysis can only begin after the ICV has been recovered within the acceptable criteria.

To assure calibration accuracy throughout each analytical run, a continuing calibration verification sample (CCV) must be analyzed at a frequency of 10% or every two hours during the analytical run, whichever is more frequent. The CCV is also analyzed after the first sample on the analytical run. If a CCV is outside the control limts, the analysis must be terminated and the analysis started back at the last CCV which was in control. If the CCV continues to fall outside of the control limits the instrument may need to be recalibrated or resloped followed by an ICV and any samples run after the last CCV which was in control will be re-analyzed. A Continuing Calibration Blank (CCB) is run after each CCV. The CCB eliminates carry over from the CCV.

The initial calibration as well as all subsequent calibrations and calibration verifications are documented.

WET CHEMISTRY DEPARTMENT

Calibration Standards

Calibration standards are prepared from high quality materials. The supplier, lot number, date prepared, expiration date and the analyst who prepared the standard are documented in the standard preparation record book. All stock solutions as well as calibration standards are labelled with, the parameter, date prepared, expiration date and the analysts initials. Stock solutions have a shelf life of no more than 1 year from preparation.

SPECTROPHOTOMETER

Calibration Procedures

An initial 5 point calibration curve is established yearly. The calibration curve acceptance criteria is a correlation coefficient of >= 0.995. Each new curve is checked against an independent standard (ICV) to verify that the curve is valid. Continuing Calibration Checks are performed at a minimum of 1 CCV per 20 samples. Each calibration curve is plotted and retained for reference. Both the initial and subsequent calibration verifications are recorded in the proper record book.

Calibration Procedures

KJELTECH

A Blank, Laboratory Control Standard and Continuing Calibration Standard are run daily. All standards and blanks are recorded in the proper record book.

TURBIDIMETER

The Turbidimeter is calibrated daily with a manufacturer known standard. Also a Laboratory Control Standard, Continuing Calibration standard and Blank are run daily. The standards and blanks are recorded in the proper record book.

BOMB CALORIMETER

The Bomb Calorimeter is checked daily with Benzoic Acid tablets. Every six months the factor is redetermined. The daily checks and factor are recorded in the proper record book.

pH METER

The pH meters are calibrated daily with two pH buffer solutions. A buffer solution from a different supplier is used to verify each daily calibration of the instrument. Continuing calibration verification standards are analyzed every 10 samples with an acceptable recovery of the standard of +/- 0.10 pH units. Both initial and subsequent calibration verifications are recorded in the proper record book.

ANALYTICAL BALANCES

All analytical balances are calibrated monthly and verified using class "S" weights. Any deviation must result in a new calibration with verification using the class "S" weights. All analytical balances receive yearly system checks and calibrations from certified technicians.

SECTION 9

Analytical Procedures

The Auburn Hills Division of NET Inc. uses a wide range of analytical methodology including US EPA approved methods for the analysis of wastewater, groundwater, drinking water, and hazardous waste. Tables 9.1 - 9.4 list the parameters, methodology, referenced method and the associated reporting limit for the metals, wet chemistry and the organics departments.

9.1 METHODOLOGY

The methodology employed by NET-Auburn Hills conforms to US EPA approved procedures as published in the Federal Register. Methods are referenced in Standard Methods for the Examination of Water and Wastewater: US EPA Manual 600/4-79- 020, "Methods of Chemical Analysis of Water and Wastes"; US EPA Manual 600/4-82-057 "Methods for Organic Analysis of Municipal and Industrial Wastewaters"; US EPA Manual SW 846, "Test Methods for Evaluating Solid Wastes"; US EPA Manual 600/4-82-057; revelant ASTM and other publications. The methodologies listed in this section are methods which are performed at a frequency greater than 120 a year. If the methods of interest are not listed in this document consult the Division Manager or the Project Managers.

9.2 REPORTING LIMITS

The reporting limits listed in this section for the parameters of interest are Practical Quantitation Limits (PQLs). The actual quantitation limits may be higher due to matrix interference or sample dilution. The PQLs for solid matrices, although using the base PQLs for aqueous matrices, are based on sample weight thus the detection levels reported will account for this weight.

NET, Inc. is in the process of updating the PQLs reported for the parameters of interest. This will be accomplished by performing method detection level studies for all parameters which this laboratory performs. The goal of NET, Inc. is to have uniform PQLs across all laboratories within the company based on the pooled results from the laboratories.

Table 9.1

Summary of Reporting Limits and Methodology
Wet Chemistry Department

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Acidity as $CaCO_3$ titrimetric	305.1 (1)	NA	4 mg/l	NA
Alkalinity as $CaCO_3$ titrimetric	403 (3)	NA	4 mg/l	NA
API Gravity	NA			
Ash	NA	D-482 (4)		
Biochemical Oxygen Demand D.O. membrane electrode	405.1 (1)	NA		
Bottom Sediment & Water (BSW)	NA	D-96 (4)		
British Thermal Units (BTU)	NA	D240-64 (4)		
Bromide Specific Ion Membrane	Br	Br	0.02 mg/l	--
Carbon Dioxide, Free CO_2 Nomographic	406A (3)	NA		
Cation Exchange Capacity Ammonium Saturation	NA	57-2.1	--	1 megr/100gr
Chemical Oxygen Demand (COD)				
Colorimetric, Manual	410.4 (1)	NA	4 mg/l	--
Titrimetric (2 levels)	410.1 (1)	410.3 (1)	--	400 mg/kg
	410.2 (1)	410.3 (1)	--	400 mg/kg
Chloride				
Titrimetric, Silver nitrate	407A (3)	407A (3)	4 mg/l	200 mg/kg
Automated Ferricyanide	325.2 (1)	NA	1 mg/l	--

Table 9.1 Cont.

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Chlorine, Total Residual DPD Colorimetric	330.5 (3)	NA	0.1 mg/l	--
Chlorine Demand Titrimetric, starch	409A (3)	NA	1 mg/l	--
Chloramines DPD ferrous titrimetric	408D	NA	0.1 mg/l	--
Coliform, fecal membrane filter	909C (3)	NA	1 col/100 mls	--
Coliform, Total membrane filter	909A (3)	NA	1 col/100 mls	--
Color Platinum Cobalt units	110.2 (1)	NA	1 unit	--
Conductivity, specific umhos 25°c	120.1 (1)	NA	2 umhos/cm	--
Cyanide, amenable Spectrophotometric	335.1 (1)	9010 (2)	0.02 mg/l	1 mg/kg
Cyanide, Total Spectrophotometric	335.2 (1)	9010 (2)	0.02 mg/l	1 mg/kg
Density Refactory Material, water displacement	NA	pt 17 C-357 (4)		
Fluoride, F Ion Selctive electrode	340.2 (1)	413A (3)	0.02 mg/l	
Flashpoint (Ignitability) Pensky Martens	NA	1010 (2)		
Hardness as $CaCO_3$ EDTA titration	130.2 (1)	NA	4 mg/l	--
Hydrogen Ion, pH electrometric	150.1 (1)	9040 (2)	--	--
Hydroxide Alkalinity (free) visual	NA	D-1093 (4)	--	--

Table 9.1 cont.

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Nitrogen, Ammonia				
Manual distillation	350.2 (1)	350.2 (1)	0.10 mg/l	25 mg/kg
followed by auto phenate	350.1 (1)	350.1 (1)	--	--
Nitrogen, Kjeldahl				
Digestion & distillation	351.3 (1)	351.3 (1)	0.50 mg/l	25 mg/kg
followed by auto phenate	351.1 (1)	351.1 (1)	--	--
Nitrogen, Nitrate				
Auto cadmium reduction	353.2 (1)	353.2 (1)	0.02 mg/l	2 mg/kg
Colorimetric, Brucine	352.1 (1)	352.1 (1)	0.02 mg/l	--
Nitrogen, Nitrite				
Colorimetric, automated	353.2 (1)	353.2 (1)	0.02 mg/l	--
Spectrophotometric	354.1 (1)	352.1 (1)	0.02 mg/l	--
Odor				
Threshold odor	140.1 (1)	NA	1 Ton	--
Oil & Grease				
Gravimetric, extraction	413.1 (1)	9071 (2)	5 mg/l	50 mg/kg
Organic Carbon, Total				
Oxidation	415.1 (1)	9060 (2)	1 mg/l	--
Organic Halogens, Total				
carbon adsorption	450.1 (1)	9020 (2)	10 ug/l	--
Oxygen, dissolved				
membrane electrode	360.1 (1)	NA	1 mg/l	
modified Winkler	360.2 (1)	NA	1 mg/l	
Paint Filter Test				
Free Liquids	NA	9095 (2)	--	--
Phenolics				
Spectrophotometric, manual 4 AAP	420.1 (1)	9065 (2)	0.002 mg/l	
Phosphorus, all forms				
colorimetric, ascorbic acid	365.2 (1)	365.2 (1)	0.02 mg/l	1 mg/kg

Table 9.1 cont.

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Reactivity				
Statement (reaction with acid/base/water)	NA	7.3.2.1 (2)	--	--
Reactive Cyanide	NA	7.3.3.2 (2)	--	--
Reactive Sulfide	NA	7.3.4.1 (2)	--	--
Solids, Total				
Gravimetric 103 - 105°c	160.3 (1)	1310 (2)	10 mg/l	0.1%
Solids, Dissolved (filterable)				
Gravimetric 180°c	160.1 (1)	NA	10 mg/l	--
Solids, Suspended (nonfilterable)				
Gravimetric	160.2 (1)	NA	4 mg/l	--
Solids, Volatile				
Gravimetric 550°c	160.4 (1)	NA	1 mg/l	0.1%
Solids, Settable				
Volumetric, Imoff Cone	160.5 (1)	NA	1 mg/l/hr	--
Sulfate				
Turbidimetric	375.4 (1)	NA	1 mg/l	--
Gravimetric	NA	9037 (2)	--	--
Sulfide,				
Colorimetric, methylene blue	376.2 (1)	NA	0.02 mg/l	2 mg/kg
Titrimetric	376.1 (1)	9030 (2)	0.1 mg/l	10 mg/kg
Sulfite,				
Titrimetric	377.1 (1)	NA	2 mg/l	--
Surfactants, MBAS				
Colorimetric	425.1 (1)	NA	0.02 mg/l	--
Sulfur				
Total Petroleum Hydrocarbons				
Gravimetric	503E (3)	503E (3)		
Extractables, IR	418.1 (1)	418.1 (1)		

Table 9.1 cont.

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Toxicity				
EP Toxicity	NA	1310 (2)		
TCLP	NA	1311 (2)		
Oily Waste Extraction	NA	1330 (2)		
Turbidity				
Nephelometric	180.1 (1)	NA	1 NTU	--
Water Content				
% by distillation	NA	D-95 (4)	--	--

Note that the above Reporting Limits are Pratical Quantitation Limits (PQL). Actual quantitation limits may be higher due to matrix interference or sample dilution. Adjustment of PQLs for solid samples are based on sample weights.

Method References:

1. EPA 600/4-79-020 "Methods for Chemical Analysis of Water & Wastes".
2. EPA SW 846, "Test Methods for Evaluating Solid Wastes".
3. "Standard Methods 16th Edition".
4. "ASTM - American Society for Testing Materials".

Table 9.2

Summary of Reporting Limits and Methodology
NET Midwest, Auburn Hills Division

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Aluminum, Al				
AA direct aspiration	202.1 (1)	202.1 (1)	1.0 mg/l	50 mg/kg
ICP	200.7 (1)	6010 (2)	0.10 mg/l	3 mg/kg
Antimony, Sb				
AA direct aspiration	204.1 (1)	7040 (2)	NA	--
ICP	200.7 (1)	6010 (2)	0.50 mg/l	25 mg/kg
Arsenic, As				
AA Hydride	206.3 (1)	7061 (2)	0.005 mg/l	0.4 mg/kg
ICP	200.7 (1)	6010 (2)	0.2 mg/l	--
AA graphite Furnace	206.2 (1)	7060 (2)	0.005 mg/l	0.10 mg/kg
Barium, Ba				
AA direct aspiration	208.1 (1)	7080 (2)	1 mg/l	--
ICP	200.7 (1)	6010 (2)	0.05 mg/l	0.5 mg/kg
Beryllium, Be				
AA direct aspiration	210.1 (1)	7090 (2)	0.01 mg/l	0.5 mg/kg
ICP	200.7 (1)	6010 (2)	0.01 mg/l	0.5 mg/kg
Boron, B				
ICP	200.7 (1)	6010 (2)	1 mg/l	50 mg/kg
Cadmium, Cd				
AA Direct Aspiration	213.1 (1)	7130 (2)	0.01 mg/l	0.5 mg/kg
AA Graphite Furnace	213.2 (1)	7131 (2)	0.001 mg/l	0.02 mg/kg
ICP	200.7 (1)	6010 (2)	0.01 mg/l	0.5 mg/kg
Calcium, Ca				
AA Direct Aspiration	215.1 (1)	215.1 (1)	0.02 mg/l	1 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg
EDTA Titration	215.2 (1)	NA	4 mg/l	--
Chromium, Hexavalent Cr+6				
AA with chelation ext.	218.4 (1)	7197 (2)	0.05 mg/l	1 mg/kg
Colorimetric, APDC	312A (3)	7196 (2)	0.05 mg/l	1 mg/kg

Table 9.2 Cont.

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Chromium, Cr				
AA Direct Aspiration	218.1 (1)	7190 (2)	0.02 mg/l	1 mg/kg
AA Graphite Furnace	218.2 (1)	7191 (2)	0.002 mg/l	0.04 mg/kg
ICP	200.7 (1)	6010 (2)	0.04 mg/l	1 mg/kg
Cobalt, Co				
AA Direct Aspiration	219.1 (1)	219.1 (1)	1.5 mg/l	--
ICP	200.7 (1)	6010 (2)	0.1 mg/l	25 mg/kg
Copper, Cu				
AA Direct Aspiration	220.1 (1)	7210 (2)	0.02 mg/l	1 mg/kg
AA Graphite Furnace	220.2 (1)	7211 (2)	0.002 mg/l	0.04 mg/kg
ICP	200.7 (1)	6010 (2)	0.01mg/l	1 mg/kg
Iron, Fe				
AA Direct Aspiration	236.1 (1)	7380 (20	0.02 mg/l	1 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg
Lead, Pb				
AA Direct Aspiration	239.1 (1)	7420 (2)	0.10 mg/l	6 mg/kg
AA Graphite Furnace	239.2 (1)	7421 (2)	0.005 mg/l	0.1 mg/kg
ICP	200.7 (1)	6010 (2)	0.05 mg/l	3 mg/kg
Lithium, Li				
AA Direct Aspiration	Li (5)	Li (5)	0.02 mg/l	1 mg/kg
Magnesium, Mg				
AA Direct Aspiration	242.1 (1)	242.1 (1)	0.02 mg/l	1 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg
Manganese, Mn				
AA Direct Aspiration	243.1 (1)	243.1 (1)	0.02 mg/l	1 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg
Mercury, Hg				
Cold Vapor, manual	245.1 (1)	7471 (2)	0.0005 mg/l	0.02 mg/kg
Molybdenum, Mo				
AA Graphite Furnace	246.2 (1)	7481 (2)	0.01 mg/l	0.20 mg/kg
ICP	200.7 (1)	6010 (2)	0.1 mg/l	25 mg/kg
Nickel, Ni				
AA Direct Aspiration	249.1 (1)	7520 (2)	0.1 mg/l	5 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg

Table 9.2 cont.

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Potassium, K				
AA Direct Aspiration	258.1 (1)	258.1 (1)	0.02 mg/l	1 mg/kg
Selenium, Se				
AA Hydride	270.3 (1)	7741 (2)	0.005 mg/l	0.4 mg/kg
AA Graphite Furnace	270.2 (1)	7740 (2)	0.005 mg/l	0.1 mg/kg
ICP	200.7 (1)	6010 (2)	0.5 mg/l	--
Silica, SiO_2				
Molybdosilicate	425C (3)		0.5 mg/l	
Silicon, Si				
ICP	200.7 (1)	6010 (2)	1.0 mg/l	50 mg/kg
Silver, Ag				
AA Direct Aspiration	272.1 (1)	7760 (2)	0.02 mg/l	1 mg/kg
AA Graphite Furnace	272.2 (1)	7761 (2)	0.001 mg/l	0.02 mg/kg
ICP	200.7 (1)	6010 (2)	0.05 mg/l	1 mg/kg
Sodium, Na				
AA Direct Aspiration	273.1 (1)	7770 (2)	0.02 mg/l	1 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg
Strontium, Sr				
ICP	200.7 (1)	6010 (2)	1 mg/l	8 mg/kg
Tantalum, Ta				
ICP	200.7 (1)9	6010 (2)	0.5 mg/l	25 mg/kg
Thallium, Tl				
AA Direct Aspiration	279.1 (1)	6010 (2)	0.5 mg/l	25 mg/kg
ICP	200.7 (1)	6010 (2)	0.5 mg/l	25 mg/kg
Tin, Sn				
AA Direct Aspiration	282.1 (1)	282.1 (1)	1.0 mg/l	50 mg/kg
ICP	200.7 (1)	6010 (2)	1.0 mg/l	50 mg/kg
Titanium, Ti				
AA Direct Aspiration	283.1 (1)	283.1 (1)	5.0 mg/l	200 mg/kg
Tungsten, W				
AA Direct Aspiration	W (5)	W (5)	10 mg/l	--
ICP	200.7 (1)	6010 (2)	1.0 mg/l	50 mg/kg

Table 9.2 cont.

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Vanadium, V				
AA Direct Aspiration	286.1 (1)	7910 (2)	0.5 mg/l	25 mg/kg
ICP	200.7 (1)	6010 (2)	0.5 mg/l	25 mg/kg
Zinc, Zn				
AA Direct Aspiration	289.1 (1)	7950 (2)	0.02 mg/l	1 mg/kg
ICP	200.7 (1)	6010 (2)	0.02 mg/l	1 mg/kg
Digestion Preparation				
Total Metals Flame	200.7 (1)	3010 (2)	NA	NA
Graphite Preparation	NA	3020 (2)	NA	NA
Oils, Greases, Waxes	NA	3040 (2)	NA	NA
Peroxide Preparation	NA	3050 (2)	NA	NA

Note that the above reporting limits are practical quantitation limits (PQL). Actual quantitation limits may be higher due to matrix interference or sample dilution. Adjustment of PQLs for solid samples are based on sample weights.

Method References:

1. EPA 600/4-79-020 "Methods for Chemical Analysis of Water & Wastes".
2. EPA SW 846 "Test Methods for Evaluating Wastes".
3. "Standard Methods 16th Edition".
4. "ASTM - American Society for Testing Materials"
5. "Atomic Absorption Methods Manual", Thermo Jarrel/Ash

Table 9.3

Summary of Reporting Limits and Methodology
Gas Chromatography (GC)

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Halogenated Volatile Organic Compounds				
Bromodichloromethane	601 (1)	8010 (2)	2ug/l	2mg/kg
Bromoform	601 (1)	8010 (2)	10ug/l	10mg/kg
Bromomethane	601 (1)	8010 (2)	5ug/l	5mg/kg
Carbon Tetrachloride	601 (1)	8010 (2)	2ug/l	2mg/kg
Chlorobenzene	601 (1)	8010 (2)	2ug/l	2mg/kg
Chloroethane	601 (1)	8010 (2)	2ug/l	2mg/kg
2-Chloroethylvinyl ether	601 (1)	8010 (2)	5ug/l	5mg/kg
Chloroform	601 (1)	8010 (2)	2ug/l	2mg/kg
Chloromethane	601 (1)	8010 (2)	5ug/l	5mg/kg
Dibromochloromethane	601 (1)	8010 (2)	5ug/l	5mg/kg
1,2-Dichlorobenzene	601 (1)	8010 (2)	10ug/l	10mg/kg
1,3-Dichlorobenzene	601 (1)	8010 (2)	10ug/l	10mg/kg
1,4-Dichlorobenzene	601 (1)	8010 (2)	10ug/l	10mg/kg
Dichlorofluoromethane	601 (1)	8010 (2)	5ug/l	5mg/kg
1,1-Dichloroethane	601 (1)	8010 (2)	2ug/l	2mg/kg
1,2-Dichloroethane	601 (1)	8010 (2)	2ug/l	2mg/kg
1,1-Dichloroethene	601 (1)	8010 (2)	2ug/l	2mg/kg
Trans-1,2-Dichloroethene	601 (1)	8010 (2)	2ug/l	2mg/kg
1,2-Dichloropropane	601 (1)	8010 (2)	2ug/l	2mg/kg
Cis-1,3-Dichloropropene	601 (1)	8010 (2)	2ug/l	2mg/kg
Trans-1,3-Dichloropropene	601 (1)	8010 (2)	2ug/l	2mg/kg
Methlyene Chloride	601 (1)	8010 (2)	2ug/l	2mg/kg
1,1,2,2-Tetrachloroethane	601 (1)	8010 (2)	2ug/l	2mg/kg
Tetrachloroethene	601 (1)	8010 (2)	2ug/l	2mg/kg
1,1,1-Trichloroethane	601 (1)	8010 (2)	2ug/l	2mg/kg
1,1,2-Trichloroethane	601 (1)	8010 (2)	2ug/l	2mg/kg
Trichloroethene	601 (1)	8010 (2)	2ug/l	2mg/kg
Trichlorofluoromethane	601 (1)	8010 (2)	2ug/l	2mg/kg
Vinyl Chloride	601 (1)	8010 (2)	5ug/l	5mg/kg
Aromatic Volatile Organic Compounds				
Benzene	602 (1)	8010 (2)	2ug/l	2mg/kg
Ethyl Benzene	602 (1)	8010 (2)	2ug/l	2mg/kg
Toluene	602 (1)	8010 (2)	2ug/l	2mg/kg
Xylenes	602 (1)	8010 (2)	2ug/l	2mg/kg

Table 9.3 Con't

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Organochlorine Pesticides				
Aldrin	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
a-BHC	608 (1)	8080 (2)	0.4ug/l	0.4mg/kg
b-BHC	608 (1)	8080 (2)	0.4ug/l	0.4mg/kg
g-BHC	608 (1)	8080 (2)	0.4ug/l	0.4mg/kg
d-BHC	608 (1)	8080 (2)	0.4ug/l	0.4mg/kg
Chlordane	608 (1)	8080 (2)	1.0ug/l	1.0mg/kg
4,4'DDD	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
4,4'DDE	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
4,4'DDT	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
Dieldrin	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
Endosulfan I	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
Endosulfan II	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
Endosulfan Sulfate	608 (1)	8080 (2)	0.8ug/l	0.8mg/kg
Endrin	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
Endrin Aldehyde	608 (1)	8080 (2)	0.8ug/l	0.8mg/kg
Heptachlor	608 (1)	8080 (2)	0.5ug/l	0.5mg/kg
Heptachlor Epoxide	608 (1)	8080 (2)	0.8ug/l	0.8mg/kg
Toxaphene	608 (1)	8080 (2)	1.0ug/l	1.0mg/kg
PCBs				
Aroclor 1016	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Aroclor 1221	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Aroclor 1232	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Aroclor 1242	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Aroclor 1248	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Aroclor 1254	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Aroclor 1260	608 (1)	8080 (2)	0.05ug/l	1.0mg/kg
Polynuclear Aromatic Hydrocarbons				
Acenaphthene	610 (1)	8310 (2)	10ug/l	10mg/kg
Acenaphthylene	610 (1)	8310 (2)	10ug/l	10mg/kg
Anthracene	610 (1)	8310 (2)	10ug/l	10mg/kg
Benzo(a)anthracene	610 (1)	8310 (2)	10ug/l	10mg/kg
Benzo(a)pyrene	610 (1)	8310 (2)	10ug/l	10mg/kg
Benzo(b)fluoranthene	610 (1)	8310 (2)	10ug/l	10mg/kg
Benzo(ghi)perylene	610 (1)	8310 (2)	10ug/l	10mg/kg
Benzo(k)fluoroanthene	610 (1)	8310 (2)	10ug/l	10mg/kg
Chrysene	610 (1)	8310 (2)	10ug/l	10mg/kg
Dibenzo(a,h)anthracene	610 (1)	8310 (2)	10ug/l	10mg/kg
Fluoranthene	610 (1)	8310 (2)	10ug/l	10mg/kg
Fluorene	610 (1)	8310 (2)	10ug/l	10mg/kg
Indeno(1,2,3-cd)pyrene	610 (1)	8310 (2)	10ug/l	10mg/kg
Naphthalene	610 (1)	8310 (2)	10ug/l	10mg/kg
Phenanthrene	610 (1)	8310 (2)	10ug/l	10mg/kg
Pyrene	610 (1)	8310 (2)	10ug/l	10mg/kg

Table 9.3 Con't

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Sample Preparation				
Liquid/Liquid Extraction	3510 (2)			
Liquid/Liquid Extraction	3520 (2)			
Soxhlet Extraction		3540 (2)		
Sonication Extraction		3550 (2)		
Waste Dilution		3580 (2)		
Purge and Trap		5030 (2)		
Alumina Column Cleanup		3610 (2)		
Florisil Column Cleanup		3620 (2)		
Silica Gel Cleanup		3630 (2)		
Gel-Permeation Cleanup		3640 (2)		
Acid-Base Partition Cleanup		3650 (2)		
Sulfur Clenaup		3660 (2)		

* Note: The Reporting Limits are based upon typical ground water samples with the listed detection limits representing the base detection level for the majority of the compounds in each parameter. Several compounds in each parameter have difference system responses and thus have higher detection levels. For details about specific compound detection levels consult the Division Manager.

Method References:

1. EPA 600/4-82-057, "Methods for Organic Analysis of Municipal and Industrial Waste Waters".
2. EPA SW-846, "Test Methods for Evaluating Solid Wastes".

Table 9.4

Summary of reporting Limits and Methodology
Gas Chromatography/Mass Spectrometry (GC/MS)

Parameter	Method Reference Water	Other	Reporting Limits Water	Other
Volatile Organic Compounds				
Acrolein	624 (1)	8240 (2)	100 ug/l	5.0 mg/kg
Acrylonitrile	624 (1)	8240 (2)	100 ug/l	5.0 mg/kg
Benzene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Bromoform	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Carbon tetrachloride	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Chlorobenzene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Chlorodibromomethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Chloroethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
2-Chloroethylvinyl ether	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Chloroform	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Dichlorobromomethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,1-Dichloroethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,2-Dichloroethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,1-Dichloroethylene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,2-Dichloropropane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,3-Dichloropropene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Ethyl Benzene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Methyl Bromide	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Methyl Chloride	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Methylene Chloride	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,1,2,2-Tetrachloroethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Tetrachloroethylene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Toluene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Trans-1,2-Dichloroethylene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,1,1-Trichloroethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
1,1,2-Trichloroethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Trichloroethylene	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Trichlorofluoromethane	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg
Vinyl Chloride	624 (1)	8240 (2)	10 ug/l	0.5 mg/kg

Table 9.4 Cont.

Summary of Reporting Limits and Methodology
Gas Chromatography/Mass Spectrometry (GC/MS)

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Semi-Volatile Organic Compounds				
Acid Compounds				
4-Chloro-3-methylphenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2-Chlorophenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2,4-Dichlorophenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2,4-Dimethylphenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2,4-Dinitrophenol	625 (1)	8250 (2)	50 ug/l	0.5mg/kg
2-Methyl-4,6-dinitrophenol	625 (1)	8250 (2)	50 ug/l	0.5mg/kg
2-Nitrophenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
4-Nitrophenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Pentachlorophenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Phenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2,4,6-Trichlorophenol	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Base Neutral Compounds				
Acenaphthene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Acenaphthylene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Anthracene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Benzidine	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Benzo(a)anthracene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Benzo(a)pyrene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Benzo(b)fluoranthene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Benzo(ghi)perylene	625 (1)	8250 (2)	25 ug/l	0.2mg/kg
Benzo(k)fluoranthene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Bis(2-chloroethoxy)methane	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Bis(2-chloroethyl)ether	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Bis(2-chloroisopropyl)ether	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Bis(2-ethylhexyl)phthalate	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
4-Bromophenyl phenyl ether	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Butyl benzyl phthalate	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2-Chloronaphthalene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
4-Chlorophenyl phenyl ether	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Chrysene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Dibenzo(a,h)anthracene	625 (1)	8250 (2)	25 ug/l	0.2mg/kg
1,2-Dichlorobenzene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
1,3-Dichlorobenzene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
1,4-Dichlorobenzene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
3,3'-Dichlorobenzidine	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Diethyl phthalate	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Dimethyl phthalate	625 (1)	8250 (2)	10 ug/l	0.1mg/kg

Table 9.4 Cont.

Parameter	Method Reference Water	Method Reference Other	Reporting Limits Water	Reporting Limits Other
Semi-Volatile Organic Compounds				
Base Neutrals Cont.				
Di-n-butyl phthalate	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2,4-Dinitrotoluene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
2,6-Dinitrotoluene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Di-n-octyl phthalate	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
1,2-Diphenylhydrazine	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Fluoranthene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Fluorene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Hexachlorobenzene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Hexachlorobutadiene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Hexachlorocyclopentadiene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Hexachloroethane	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Indeno(1,2,3,-cd)pyrene	625 (1)	8250 (2)	25 ug/l	0.2mg/kg
Isophorone	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Naphthalene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Nitrobenzene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
N-Nitrosodimethylamine	625 (1)	8250 (2)	100 ug/l	1.0mg/kg
N-Nitroso-di-n-propylamine	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
N-Nitrosodiphenylamine	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Phenanthrene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
Pyrene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg
1,2,4-Trichlorobenzene	625 (1)	8250 (2)	10 ug/l	0.1mg/kg

* Note: The Reporting Limits are based upon typical ground water samples with the listed reporting limits representing the base detection level for the majority of the compounds in each parameter. Several compounds in each parameter have different system responses and thus have higher detection levels. For details about specific compound detection levels consult the Project Manager.

Method References:

1. EPA 600/4-82-057, "Methods for Organic Analysis of Municipal and Industrial Waste Waters".
2. EPA SW-846, "Test Methods for Evaluating Solid Waste".

SECTION 10

Data Reduction, Validation, and Reporting

Data Reduction

Analytical results are reduced to appropriate concentration units which are dictated by the analytical method. Where required by method, blank correction will be applied. Calculations will be independently verified by appropriate laboratory staff.

Calculations

All raw data are recorded in notebooks or on sample benchsheets never on scraps of paper. These data are then used to calculate the value. If calculations are needed they are written in the front of the notebooks with any factors also indicated. All values reported are to be rounded correctly (see Rules for Rounding) to the correct significant figures.

Significant Figures

The values obtained or calculated often have more digits than can be justified by method accuracy or precision. These values are to be rounded to the number of significant figures that can be confidently reported. The definition of significant figure is the number of digits remaining once the data is rounded. The last, or last two digits, should be the only ones which may change upon further analysis.

Any zeros used to locate the decimal point are not counted as significant figures (ie. 0.0035 has two significant figures). All zeros to the right of a digit are not considered significant unless a decimal point is placed after them (ie. 3500 has two significant figures while 3500.0 has five significant figures). Due to this, care should be taken when adding zeros and decimal points to values.

Rules for Rounding

The following rules are to be followed by all laboratory personnel when rounding data to the correct significant figures:

1. When the digit immediately after the one to be retained is less than five, the retained figure is kept unchanged. For example: 2.541 becomes 2.5 to two significant figures.

2. When the digit immediately after the one to be retained is greater than five, the retained figure is increased by one. For example: 2.453 becomes 2.5 to two significant figures.

3. When the digit immediately after the one to be retained is exactly five and the retained digit is even, it is left unchanged and conversely. For example: 3.450 becomes 3.4, but 3.550 becomes 3.6 to two significant figures.

4. When two or more figures are to the right of the last figure to be retained, they are considered as a group in rounding decisions. Thus in 2.4501, the group (501) is considered to be >5 while for 2.5499 the group (499) is considered to be <5.

Data Validation

Data validation is the process of evaluating data and either accepting or rejecting it based upon a set of criteria. NET analysts and supervisors validate laboratory data with the use of the following criteria:

- proper sample collection
- a complete Chain of Custody
- use of Standard Operating Procedures or other approved analytical procedures
- use of properly operating and calibrated instruments
- precision and accuracy comparable to that obtained in similar analytical programs

Records on all data will be maintained. These records include the chromatograms, strip charts and laboratory notebooks. Persons validating the data will have a sufficient knowledge of the technical work to identify questionable values.

Data Reporting

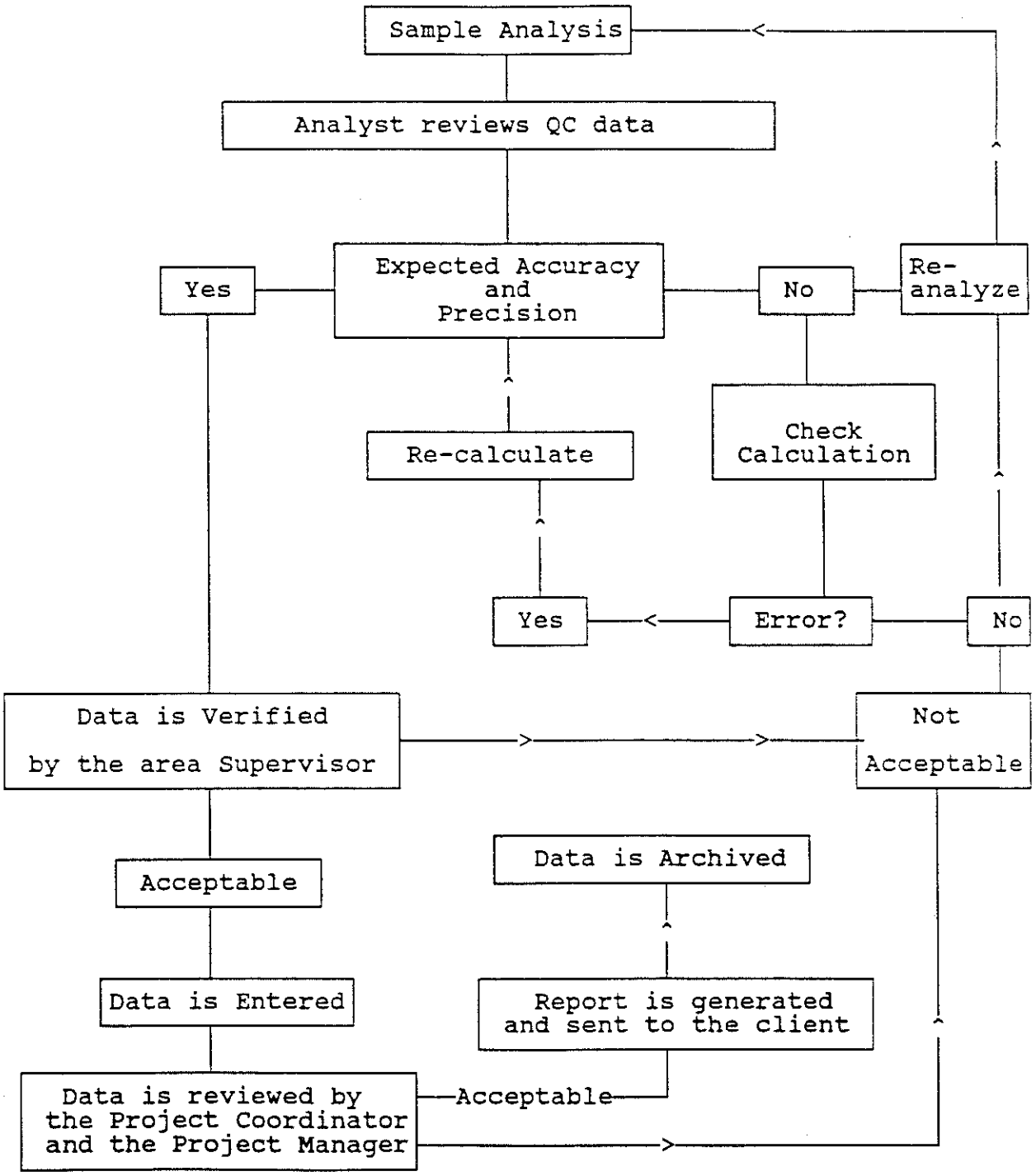
All reports will be assembled and approved by a Project Management Team, and delivered to the client within a timely manner and in an acceptable format.

Any additional information required by the client, such as operating conditions, QA/QC data, recommendations, method citations or problems will be reported by the Project Manager.

Occasionally a report must be re-issued due to the addition of a test(s). A letter is sent to the client along with the re-issued report explaining the reason for the re-issue.

Figure 10.1 shows the analytical data reporting scheme from analysis to archival of analytical results.

Figure 10.1 Analytical Data Reporting Scheme



SECTION 11

Internal Quality Control and Frequency

INTERNAL QUALITY CONTROL

Internal quality control makes use of several types of QC samples to monitor the performance of the measurement process. Quality control checks are analyzed to ensure the generation of valid data for client samples. Below is a list of the types of QC samples used in the laboratory.

Procedure Blank

A DI water sample that is prepared in the laboratory just like a sample. The method blank is analyzed with samples that were processed at the same time as the blank. The method blanks are used to assess the extent of contamination, if any, obtained during the preparation process.

Solvent/Reagent Blank

A blank prepared from any solvent or reagent lot used in the analysis. This blank is used to assess any background contamination due to the solvents/reagents.

Initial Calibration Verification Standard (ICV)

The calibration of an instrument is checked with this standard prepared from a source other than that used to calibrate the instrument. An ICV is analyzed after each new calibration of an instrument.

Continuing Calibration Verification (CCV)

During the analytical run, at a minimum frequency of one CCV per 20 samples, the mid-range calibration standard is re-analyzed to assess the calibration of the instrument.

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A sample is split into three aliquots. One aliquot of the sample is set aside. The other two aliquots are spiked with a known concentration of the analyte(s). All three aliquots are prepared in the same manner and analyzed in the same analytical batch. Precision can then be determined by comparing the result of the matrix spike/matrix spike duplicate (MS/MSD) pair. Accuracy can be determined from the matrix of interest by calculating the recovery of the spiked analytes.

Duplicate Analysis

For those analytes which cannot be spiked (ie. pH), two aliquots of the sample are analyzed. The results of the two analyses are compared to determine precision. Duplicate analysis is carried out at a minimum frequency of 1 per 10 samples or per batch, which ever is less.

Tune Check

GC/MS instruments analyze BFB (4-Bromofluorobenzene) for volatiles or DFTPP (Decafluorotriphenylphosphine) for semi-volatiles to tune check. The mass spectrum of the appropriate compound is produced every 12 hours or every 8 hours in the case of Method 524.2. The ions produced in this spectrum must pass all of the Method specifications.

Surrogate Compounds (Organic Analysis)

Samples have surrogate compounds added to them before sample preparation. Surrogate compounds are chemically similar to the analytes being measured. Surrogates are used to assess the behavior of the analytes with the matrix, during sample preparation and analysis. Surrogate compounds must meet all method specifications.

Internal Standards (GC/MS)

Internal standards are pure compounds added to each standard and sample in known amounts to measure the relative response of method analytes. Each internal standard represents a group of analytes. The internal standard is used in conjunction with the calibration standards to determine analyte concentration. Internal standards are added immediately before analysis. Internal standard peak areas must meet all method specifications.

Laboratory Control Standard (LCS)

The LCS is a standard that is prepared along with a group of client samples. This standard is also analyzed along with the batch of samples to which it belongs. The accuracy of the preparation procedure can be assessed by determining the percent recovery of the analyte(s) in the standard.

Reporting Limit Verification Standard (RLVS)

A standard prepared at the reporting limit for the analyte of interest is used to assess the validity of the current reporting limit when the calibration curve does not include a standard at the reporting limit. This demonstrates that the reporting limit is an achievable quantity.

The quality assurance measures and their frequency are described below. Control limits for the QC samples are summarized in Tables 5.1 - 5.12.

Metals Analyses

Procedure Blanks - Procedure Blanks are carried through the sample preparation at a frequency of one per batch of 20 samples per matrix.

Laboratory Control Standard - A LCS is carried through the sample preparation at a frequency of one per batch of 20 samples per matrix. All analytes represented in a given analytical batch will have the LCS analyzed for that metal.

Matrix Spike/Matrix Spike Duplicate - One MS/MSD is represented in each digested batch of samples which contain a maximum of 20 samples. The MS/MSD is analyzed for all of the metals represented in the analytical batch.

Calibration - A three point curve is analyzed at the beginning of each analytical run.

Initial Calibration Verification Standard - Each analytical run will have an ICV analyzed immediately after each daily calibration.

Reporting Limit Verification Standard - If the low standard in the calibration curve is not at the reporting limit then the RLVS is analyzed at the beginning of each analytical run.

Reagent Blank - Analyzed at the beginning, every tenth sample and at the end of the analytical run.

Continuing Calibration Verification Standard - Analyzed every tenth sample throughout the analytical run. Each analytical run will also end with a CCV.

Wet Chemistry Analyses

Titrations:

- Reagent Blank - Run with each analytical run
- ICV - Analyzed from an alternate source once with each analytical run.
- CCVs - Analyzed at the beginning and the end of the analytical run.
- MS/MSDs - Analyzed if possible every 20 samples.
- Duplicates - If spiking is not possible every 10 samples or one per analytical batch is duplicated.

Spectrophotometric Parameters:

- Reagent Blank - If necessary, one per analytical run is analyzed and every 20 samples.
- ICV - Analyzed from an alternate source once with each new calibration.
- Procedure blank - Analyzed once with each batch of samples requiring a preparation/digestion.
- CCVs - Analyzed at the beginning, every 20 samples and the end of the analytical run.
- MS/MSDs - Analyzed every 20 samples or per analytical batch if less than 20 samples.

Gravimetric Parameters:

- Procedure Blank - Analyzed once with each analytical batch.
- Standard - Analyzed every 20 samples or per analytical batch if less than 20 samples.
- Duplicate - Analyzed every 10 samples or per analytical batch if less than 10 samples.

Digestions/Preparations/Distillations/Extractions:

- Procedure Blank - Set up with each analytical batch.
- LCS - Set up with each analytical batch.
- MS/MSD - Set up with each analytical batch per matrix.

(Batch = all samples that can be set up in one day not to exceed 20 samples.)

GC/MS Organic Department

- Procedure Blank - Analyzed with each extraction batch.
- Tune Check - Bromofluorobenzene or DFTPP analyzed at the beginning of each 8 or 12 hour run sequence depending upon the method being used.
- ICV - Analyzed with each new calibration curve
- CCV - CCC compounds analyzed after each successful tune for each analytical run sequence.
- Surrogates - Added to each sample and blank and analyzed with each sample.
- MS/MSD - One in every 20 samples.
- LCS - Analyzed one in every batch.

GC Organic Department

Methods 608/8080/PCBs and Pesticides

- Procedure Blank - Analyzed with each extraction batch.
- ICV - Analyzed with each new calibration curve.
- CCV - Analyzed every ten samples on the analytical run sequence.
- Surrogate - Added to each sample and blank and analyzed with each sample.
- MS/MSD - One in every 20 samples.
- LCS - Analyzed one in every batch.

Method 604

- Procedure Blank - Analyzed with each extraction batch.
- ICV - Analyzed after each new calibration curve.
- CCV - Analyzed at the beginning, every 10 samples and at the end of the analytical run.
- MS/MSD - One in every 20 samples.
- LCS - Analyzed one in every batch.

Method 610/8310

- Procedure Blank - Analyzed with every extraction batch.
- ICV - Analyzed after each new calibration curve.
- CCV - Analyzed every 10 samples.
- Surrogate - Added to all samples and blank and analyzed on each analytical run.
- MS/MSD - One in every 20 samples.
- LCS - Analyzed one in every batch.

Method 601/8010/602/8020

- Procedure Blank - Analyzed with every analytical batch.
- ICV - Analyzed with each new calibration
- CCV - Analyzed every 10 samples and at the end of the analytical run.
- Surrogate - added to all samples and blank and analyzed on each analytical run.
- MS/MSD - One in every 20 samples.

Methods 8150

- Procedure Blank - Analyzed with every extraction batch.
- ICV - Analyzed after each new calibration curve.
- CCV - Analyzed at the beginning, every 10 samples and at the end of each analytical run.
- MS/MSD - One in every 20 samples.
- LCS - Analyzed one in every batch.

SECTION 12

Performance and Systems Audits

PERFORMANCE AUDITS

The QA objective of the Auburn Hills Division is to provide data of known and documented quality. To this end, the Auburn Hills Division participates in several performance evaluation audits as well as NET's own Interlaboratory Testing Program (ITP).

The external performance evaluation audits and round robins that Auburn Hills participates in are briefly described below.

EPA Water Pollution (WP) Performance Evaluation Audit Program: The U.S. EPA distributes ampules containing unknown concentrations of a wide variety of organic and inorganic parameters. The analyses are made by the laboratory personnel using routine analytical procedures. After evaluation by the EPA, NET Midwest receives a listing of true concentrations of each analyte. This program monitors laboratories which perform analyses on NPDES and POTW pre-treatment agreement samples. This performance evaluation audit is conducted on a semi-annual basis.

EPA Water Supply (WS) Performance Audit Program: A program similar to the EPA WP performance evaluation audit, except this program monitors laboratories which perform analysis for the Safe Drinking Water Act parameters. This audit is conducted on a semi-annual basis.

Chemical Waste Management Round Robin: This program consists of quarterly analyses conducted on waste matrices for various inorganic and organic constituents. True values for each analysis are supplied by Chemical Waste Management after the performance evaluation data has been reviewed. Annual on-site systems audits are performed by Chemical Waste Management Quality Assurance Auditors per the request of Waste Management. This laboratory has maintained an approval status for the characterization of waste samples for RCRA hazardous characteristics criteria.

INTERNAL SYSTEMS AUDITS

The system audit is a systematic check of a qualitative nature consisting of a review of a laboratory's quality assurance systems and physical facilities for sampling, calibration and measurements. System audits are conducted on a regular basis by the QA Coordinator in six areas within the Auburn Hills Division of NET Midwest. These departments are: Wet Chemistry, Metals, GC, GC/MS, Field Sampling and Office/Login.

These audits include several components listed below:

- Personnel, facilities and equipment
- Chain of custody procedures
- Instrument calibration and maintenance
- Standards preparation and verification
- Analytical procedures
- Quality control procedures
- Data handling procedures
- Documentation control procedures

CERTIFICATIONS

The Auburn Hills Division maintains several certifications. Analytical services that require laboratory certification which NET Auburn Hills does not currently hold, (such as industrial hygiene monitoring) may be obtained through the NET network of laboratories.

Current Certifications at NET Auburn Hills include:

State of Michigan Department of Public Health Drinking Water Certifications for the following analytes.

Inorganics:

Cyanide	Lead	Copper	Nickel
Fluoride	Sodium	Mercury	
Nitrate	Barium	Selenium	
Nitrite	Cadmium	Silver	
Sulfate	Chromium	Beryllium	

Organics:

Endrin	Methoxychlor
Lindane	Silvex 2,4,5-TP

Bacteriological:

Total Coliform

SECTION 13

Preventative Maintenance

Preventative maintenance procedures such as lubrication, detector cleaning and the frequency of such maintenance are performed according to the procedures outlined in the manufacturer's manual. Precision and accuracy data are examined for trends beyond control limits to determine evidence of instrument problems. Maintenance must be performed when instrument performance begins to deteriorate as made evident by poor peak resolution, shifts in calibration curves, loss of sensitivity, or failure to meet one of the quality control criteria.

Instrument notebooks are kept containing usage, calibration, maintenance and repair record/agreements. The laboratory maintains adequate supplies of selective spare parts for use as needed.

In the event of equipment failure that cannot be resolved in-house, service is performed by instrument manufacturer, or a certified technician. If on-site repair is not possible, then arrangements are made to ship the instrument back to the manufacturer for necessary repairs. See Table 13.1 for a list of common maintenance procedures for major instrumentation.

Table 13.1
Maintenance Procedures for Major Instrumentation

Instrumentation	Maintenance Procedure	Spare Parts
Gas Chromatography/ Mass Spectrometry	1. Replace pump oil as needed 2. Change septa as needed 3. Change gas line dryers as needed 4. Clean source as needed 5. Replace electron multiplier as needed 6. Injection Port Cleaning as needed	1. Syringes 2. Septa 3. Various electronic components 4. Plumbing supplies
Gas Chromatograph	1. Change septa as needed 2. Change gas line dryers as needed 3. Change syringes on auto-samplers as needed 4. Leak check when installing new columns 5. Check inlet system for residue buildup periodically 6. Change injection port liner as needed	1. Septa 2. Syringes 3. Injection port liner 4. Various electronic components 5. Plumbing supplies
Purge and Trap Sample Concentrator	1. Replace trap as needed 2. Decontaminate system as determined from blank 3. Leak check system	1. Spare trap 2. Various electronic components 3. Plumbing supplies
Graphite Furnace Atomic Absorption Spectrophotometer	1. Change graphite contact as needed 2. Change D2 background correction lamp as needed 3. Clean quartz windows as needed	1. Contact rings 2. D2 lamp
Flame Atomic Absorption Spectrophotometer	1. Change contact rings as needed 2. Replace nebulizer components 3. Clean lamp and compartments	1. Contact rings 2. Nebulizer components 3. Lamps
Kjeltech	1. Clean Alkali Tank 2. Check Refill Alarm 3. Check Alkali Volume 4. Clean titration vessel	1. Lamps 2. Floatswitch 3. Rubber Adaptor 4. Splash Head

SECTION 14

Specific Routine Procedures to be Used to Assess Data Precision, Accuracy and Completeness of Specific Measurement Parameters

PRECISION

A precision analysis is a duplicate analysis of a sample or of a matrix spike. The duplicate goes through the same preparation procedures as the samples. Precision analysis is carried out according to the frequencies described in Section 11.

Determination of Precision

Precision is determined by calculating the Relative Percent Difference (RPD). For duplicate analysis relative percent difference calculations are carried out on the original and duplicate analyses. For Matrix Spike/Matrix Spike Duplicates the relative percent difference calculations are carried out on the Matrix Spike/Matrix Spike Duplicate pairs. Equation 14.1 is the calculation for relative percent difference:

Equation 14.1 $$RPD = \frac{(R1) - (R2)}{(R1 + R2)/2} \times 100$$

R1 = Original Sample or Matrix Spike Result
R2 = Duplicate Sample or Matrix Spike Dup Result

ACCURACY

Accuracy analysis is carried out on a sample which has been spiked with a known concentration of analyte. This spiked sample is then prepared and analyzed as if a true sample. Accuracy analysis is carried out at a minimum frequency of 1 in 20 samples (unless stated at a different frequency in the analytical method). The Laboratory Control Standard and Standard Reference Material are also used to indicate accuracy. The accuracy value is reported as the percent recovery of the spike. Equation 14.2 is the calculation for the % Recovery in the MS or MSD.

Equation 14.2 $$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} \times 100$$

SSR = Spiked Sample Result (Sample concentration for MS/MSD's)

SR = Original Sample Result (Sample concentration for MS/MSD's)

SA = Spike Concentration Added (or MS concentration for MS/MSD's)

COMPLETENESS

Completeness is the amount of valid data obtained from the analytical measurement system. It is defined as the total amount of acceptable data divided by the total number of samples received multiplied by 100. The QA objective for this QA Plan is to obtain acceptable data for all of the samples received. The procedures in section 10 of this QA plan for validating data will be used to determined which data are acceptable. Completeness also implies the ability of the final report to answer the client's questions. Equation 14.3 is used to determine Completeness.

Equation 14.3 $$C = \frac{V}{T} \times 100$$

C = Percent Completeness
V = Number of Measurements Judged Valid
T = Total Number of Measurements

SECTION 15

Corrective Action

A quality assurance program cannot be considered complete without a defined and usable policy for correcting quality problems. NET utilizes a closed-loop corrective action system which is directed by the Division Manager and the Quality Assurance Coordinator. The quality assurance program is designed to avoid problems but it also is used to identify potential problems and to identify and correct any problems that may exist. Quality control problems fall into two categories: those requiring immediate corrective action or those which require long-term corrective action.

The quality control procedures outlined to this point in the manual are designed to help analysts detect the need for corrective action. Often the analyst's previous experience will be the most valuable tool in identifying suspicious results or malfunctioning equipment; immediate corrective action can then be taken. The actions taken or suspect data are noted in the laboratory notebook but further documentation is not necessary unless further corrective action will be needed.

Long-term corrective action is identified by standard QC procedures, control charts, performance or systems audits. Any quality issue that cannot be solved by immediate action requires long-term corrective action. NET uses a system to ensure that the condition is reported to a person who is part of the closed-loop action and follow-up plan. Figures 15.1 through 15.3 show the forms used by NET to track corrective action.

As part of the quarterly systems audits in each department, previous findings requiring corrective action are investigated during the next audit to determine if the corrective action taken on the earlier problem is still being used consistently.

The essential steps of the closed loop corrective action system are:

1. Identify the problem
2. Assign responsibility for investigating the problem
3. Investigate and determine the cause of the problem
4. Determine a corrective action to eliminate the problem
5. Assign responsibility for implementing the corrective action.

6. Implement the corrective action.

7. Verify that the corrective action has solved the problem by running either a double or single blind performance evaluation sample.

8. Document and archive the entire corrective action process.

All long-term corrective actions, once identified, are followed through the closed loop system by the QA Coordinators. The Division Manager has the ultimate responsibility to see that the prescribed corrective action is operational and has solved the problem.

Figure 15.1 Part One ITP Corrective Action Report.

NATIONAL ENVIRONMENTAL TESTING, INC.

Corrective Action Report

DATE:

TO: QA Director cc:

RE: Out-of-Control ITP Value Reported

FR: _____

Division: _____ Dept: _____

Analysis: _____ ITP#: _____

True value: _____ Reported value: _____ Units: _____

Control limits (CLs): _____ CL ref: APG; 2*stdev

Method reference & #: _____

Instrument ID and type: _____

Problem Identification - Check ALL Boxes That Apply

☐ Training	☐ Supervision
☐ Method not followed	☐ Login
☐ QC not performed	☐ Reporting
☐ QC CLs ignored	☐ Laboratory contamination
☐ Detection limits problems	☐ Instrument or service problem
☐ Dilution or calculation	☐ Standards supplier problem
☐ Other _____	☐ Unknown

Corrective Action Taken: 1. _____

_____

_____

_____

Date: _____ _____
Section Supervisor

_____ _____
QA Manager Division Manager

Figure 15.2. Part One of ITP Corrective Action Report.

Corrective Action Report - Quality Control Indicators

ITP#:_____ Anaylsis:_____ Division:_____

DETECTION LIMIT (DL)	METHOD BLANK
Date run Measured DL	Date Concentration Control Limit(CL)
_____ _____	_____ _____ _____
Detection Limit Reference	Method Blank CL Reference
_____	_____

EXTERNAL STANDARD VERIFICATION - INDEPENDENT REFERENCE

Date run	True Concentration	Measured Concentration	CLs
_____	_____	_____	_____

External Standard Control Limit Reference

_____

CONTINUING CALIBRATION VERIFICATION-ON-GOING CALIBRATION CHECK

Date run	True Concentration	Measured Concentration	CLs
_____	_____	_____	_____

LCS Control Limit Reference

_____

ACCURACY CHECK - SAMPLE SPIKE

Date run	Sample Conc.	Spike Conc. Added	Total Conc. Observed	Percent Recovery
_____	_____	_____	_____	_____

Accuracy CLs Accuracy Control Limit Reference

_____ _____

PRECISION CHECK - SPIKE & SPIKE DUPLICATE OR SAMPLE & DUPLICATE

Date run	True Conc.	Relative % Difference (RPD)	RPD CL	RPD CL Reference
_____	_____	_____	_____	_____

CALIBRATION

Date run	# of standards	Lowest standard Concentration	Highest standard Concentration
_____	_____	_____	_____

Calibration CL Observed Calibration CL Reference

_____ _____ _____

_____ _____

SIGNATURE DATE

Figure 15.3. Part Two ITP Corrective Action Report.

NATIONAL ENVIRONMENTAL TESTING, INC.

Corrective Action Report Part Two

DATE:

TO: QA Director

cc:

RE: Regionally Administered PE Results

FR: Regional Quality Assurance Manager

ITP#:_____ Analysis:_____ Division:_____

PE Sample Source: _____

PE True Value: _____ PE Control Limits: _____

Control Limit reference: _____

Laboratory Result: _____

Date of PE Analysis: _____

Was the PE Single Blind? _____ Double Blind? _____

Is the Analysis now in Control: _____

Comments: _____

_____

_____

_____

_____

_____

_____

Regional Quality Assurance Manager

SECTION 16

Quality Assurance Reports to Management

In order to provide information to the Division Manager concerning the performance of the laboratory in the quality assurance program, the QA Coordinator will meet with him on a weekly, or as needed, to review quality control data trends, problems and other information.

The information in these meetings is then summarized and disseminated to the Project Managers and the other Departmental Supervisors.

The QA Coordinator is also given the opportunity during weekly staff meetings to discuss any QA issues which are of immediate concern. This forum is also used to remind Supervisors of Performance Evaluation Studies for which analyses have yet to be completed.

QA Reports made directly to the Director of Data Quality concern Performance Evaluation results, Corrective Action Reports and QA Summaries (staff meeting notes).

ATTACHMENT 11B

STATISTICAL TESTING METHODS

ATTACHMENT 11B

Statistical Testing Methods

11B.1 Introduction

This section describes the general procedures for determining if changes in the concentrations of detectable constituents in the various environmental monitoring systems at the landfill are statistically significant. The test for statistical significance is required under Part 111 of Act 451 and by its inclusion by reference in the federal regulations in 40 CFR Part 264, Subpart F. Tests for statistical significance in the leak detection system of Cell II are required by Michigan Department of Natural Resources (MDNR) policy under Part 111 of Act 451. Statistical procedures are used to provide an objective evaluation of the significance of changes in the chemical data collected from the various monitoring systems present at the site. In combination with the leak detection system, the statistical evaluation provides an early warning system for the landfill. Specific statistical procedures to be followed are presented in the Monitoring Plans and Procedures for each environmental media. This Attachment provides an overview of the statistical approaches to be followed.

In addition to the above-referenced regulations, the statistical tests proposed here were chosen to be consistent with the background data collected at the site from the time Cell II was first permitted in 1988, and the guidelines presented in the MDNR Cleanup Verification Guidance Document (MDNR, 1991), and the USEPA Guidance Document on the Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities (USEPA, 1989 and USEPA, 1993).

11B.2 Overview of Statistical Procedures

The choice of statistical procedures is necessarily based on the characteristics of the data being evaluated. Ford Motor Company is proposing a series of statistical methods that will be selected from for each media based on the specific characteristics of the particular data set. Important characteristics include the statistical distribution and the degree of censoring in the data. The selection of the appropriate method for each data set will be made after the completion of the background data collection program. Changes to the statistical evaluation plan will be made only with the MDNR's approval.

11B.3 Selection of Parameters for Statistical Evaluation and 100 Percent Censored Data

Repeated use of a statistical test during successive monitoring events can lead to a significant chance that a false-positive (Type I error) result may occur. The USEPA Guidance Document on the Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities (USEPA, 1993) states "...when the number of comparisons is moderate to large the false positive rate associated with the testing network as a whole (that is, across all comparisons involving a separate statistical test) can be quite high. This means that, if enough tests are run, there will be a significant chance that at least one test will indicate contamination, even if no actual contamination has occurred." The guidance document goes on to suggest that, in order to reduce the false-positive rate associated with a statistical program, only those constituents that are likely to be reliable indicators of potential contamination should be statistically tested on a regular basis.

In order to reduce the Type I error rate, several indicator parameters have been selected for statistical evaluation (chrome, copper, arsenic, selenium, and volatile and semi-volatile organic compounds). These parameters were chosen based upon the anticipated waste streams at Cell II. The analytical parameters for which statistics are performed will be evaluated annually in conjunction with the annual review and revision of the monitoring parameter list (see Subsection 11.5.1). If the waste accepted for disposal at the landfill changes, or if the results of leachate monitoring indicate that other parameters analyzed for would be more representative indicators of environmental impacts, then the statistical program may be changed with the approval of the WMD.

Similarly, statistical analysis of parameters that have background data sets that are 100 percent nondetect is not appropriate. If any of the parameters selected for statistical analysis, as listed above, have background data sets that are 100 percent censored, then the actual level of detection will act as a trigger for resampling. An operational monitoring sample result that exceeds the analytical detection limit will be confirmed by collecting an individual sample at that location and analyzing for the parameter that exceeded background. This measure is being taken in order to rule out laboratory error as a source of the detection. If the analyte is not detected in the confirmatory sample, then no further action will be taken. If the analyte is detected, then the location will be resampled in quadruplicate, and the resampling data will be evaluated using the statistical procedure appropriate for the percentage of nondetects in the results, as described in the Monitoring Plan and Procedures document for the media sampled.

11B.4 General Statistical Methods

The following steps will be followed in carrying out statistical evaluations. The steps described below will be followed for the first round of statistical evaluation. Subsequent rounds will not require evaluation of background data. Each procedure is described in detail for each environmental media (soil, sediment, surface water, leak detection system, lysimeters) in the Monitoring Plan and Procedure document for each media.

1. Tabulate, evaluate, and reduce the existing background data.

2. Revise, if necessary, the estimated quantitation limits (RDLs) for each constituent.

3. If the background data set is 100 percent censored, then do not perform statistics. The actual level of detection will serve as the trigger value for resampling, as described above.

4. Assess the underlying statistical distribution of the data, and correct for log normality if necessary. After the first round of statistical evaluation has been completed, this step will consist of transforming the current data, if necessary, based on the previous evaluation.

5. Inspect the data set for outliers, and remove or revise outliers found to be in error.

6. Inspect the current round of data for nondetects. If a parameter was reported to be below the RDL for that round, then do not perform a statistical test with that data (i.e., do not perform a statistical evaluation to determine if a nondetect represents an exceedance of background).

7. Evaluate the degree of censorship in the data, and select the appropriate statistical test based on this evaluation.

8. Perform the statistical test identified in step 7 to determine if a statistically significant difference from background has occurred.

11B.5 Background Data Evaluation

The existing background data collected by Ford Motor Company were combined to produce a computer file data base. The data were reviewed to determine completeness and to determine if sample locations were consistent and clearly defined. A review of the data base showed that the requirements for background monitoring, as defined by the existing operating license, could be met with the available data. Because new monitoring parameters will be added, an additional background monitoring program has been included (described in Section 11). The additional background data will be evaluated in the same manner when background data collection is completed.

11B.6 Determination of RDLs

Analytical data are often censored, meaning that parameters are often listed as being below the reportable detection limit (RDL) of the method. While not useful in a quantifiable sense, censored data can provide qualitative information concerning the chemical makeup of a sampled media. RDLs are typically matrix and laboratory specific and provide information on the ability of an analytical method and an analytical laboratory to measure parameters to a specific, lower concentration or value.

A problem often encountered in developing background data sets for environmental monitoring produced from data analyzed over time, or produced from analysis of highly variable solutions such as leachate, is that the RDLs reported by analytical laboratories may change with time. Typically, RDLs decrease as analytical procedures and techniques improve. Variable RDLs present statistical problems in producing average values if corrections are used for censored data. A review of the existing background data set showed that variations in RDLs occurred for several parameters in the data set. To calculate meaningful test values, the largest detection limit for each parameter was used wherever a correction for censored data was needed. Using the largest reported RDL value for each constituent is appropriate because the maximum value sets the level of accuracy that can be attained in future monitoring, even if RDLs decrease in the future. Procedures used to correct for censored data are described below.

11B.7 Evaluation of Underlying Data Distribution

Statistical tests used to evaluate environmental monitoring data are typically based on the assumption that samples are drawn from a normally distributed population (i.e., parametric statistics are appropriate). However, geochemical data are often found to be log-normally distributed, or more typically, a mixture of log and normally distributed values. Applying parametric statistics to non-normally distributed data can lead to numerous errors, including high rates of false positives when making comparisons against background values.

For meaningful statistical comparisons to be made, the underlying distribution of each parameter measured in the various matrices must be determined, and if necessary, correction must be made for log-normality. The background data provide insight into the statistical distribution expected for the operational monitoring data.

The background data set for each sampling point for each parameter that is a part of the statistical evaluation program will be assessed to determine the underlying distribution of the data. As recommended in the February 1993 USEPA Guidance document, normality of the data will be assessed by constructing probability plots (see page A11-B-10). This method will be used because most tests for normality do not have a high degree of statistical power when the sample size is small, and most of the background data sets to be evaluated will be of a sample size of less than ten samples.

A probability plot is constructed by plotting observed values in increasing order on the x-axis, and the proportion of observations less than or equal to each observed value is plotted as the y-coordinate. The plotted points will approximate a straight line if the data are normal. Because environmental concentration data are often log-normally distributed (USEPA, 1993), probability plots of the log-transformed and the raw data will be constructed for each parameter. The plots will be compared and a decision will be made as to which representation of the data is closer to the normal distribution. If the log-transformed data are selected as appropriate, all background and operational data for that sample point for that parameter will be transformed prior to conducting any statistical tests on the data. All reports of the statistical evaluation of the data will state whether the statistical test was conducted on raw or transformed data.

11B.8 Outlier Correction

Testing for outlier values was performed on all parameters in the background data set to help identify potentially erroneous values (see page A11-B-21). The test was performed according to the procedures detailed in the Monitoring Plan and Procedures for each parameter tested. The background data set was found to contain many possible outlier values, especially for the liquid matrices such as leachate. However, because no information was found that suggested the cause of the spurious data (other then the data represent natural variation), all data were used to develop background concentrations.

Subsequent operational monitoring data will be tested for outliers using the same method. If identified as having outliers, then the operational monitoring data may be corrected or removed from the data set **only** if the outlier value can be identified as:

(1) an error in transcription or dilution;

(2) a documented error in an analytical procedure or report of matrix interferences in the procedure; or

(3) some other factor from those listed in the RCRA guidance (USEPA, 1989).

In the event an outlier can be verified, the MDNR's permission will be obtained before the outlier is removed from the data set. If no obvious cause can be identified for a value being an outlier, it will remain in the operational data set used for statistical evaluation unless the MDNR's approval is obtained to remove it.

11B.9 Inspection for Nondetects

If a parameter that is a part of the statistical evaluation program is reported to be below the RDL for a sampling point during a round of sampling, then a statistical test will not be performed on that result. The analytical result will be added to the database for that sample point. This approach is being taken because it is reasonable to assume that a nondetect cannot represent an exceedance of background.

11B.10 Select and Perform the Appropriate Statistical Test

The following steps will be followed to determine how censored data will be handled and to select the statistical test to be performed for each parameter at each sampling point:

a) If the percentage of nondetects in the database for the sample point is less than 15 percent, then substitute a value of 1/2 the RDL for all nondetects in the background and monitoring data sets and calculate a prediction interval (see page A11-B-32). Prediction intervals may be used to compute an inter-point comparison between a monitoring point and a background location, and to compute an intra-point comparison between background and compliance monitoring data from the same location. In order to perform an intra-point comparison, the background data set must be obtained when the monitoring point is known to be uncontaminated.

b) If the percentage of nondetects in the database for the sample point is between 15 and 50 percent, then use Cohen's or Aichison's adjustment to calculate the mean and standard deviation of the background data. Use these adjusted statistics to calculate a prediction interval (see page A11-B-43).

c) If the percentage of nondetects in the database for the sample point is between 50 and 90 percent, then use the Wilcoxan Rank-Sum Test to compare operational monitoring results to background data (see page A11-B-58). Although nonparametric prediction intervals may be used in this case, the false-positive rate associated with nonparametric prediction interval depends on

the number of background data available (see page A11-B-69). For example, in cases where six background data points are available, the error rate associated with nonparametric prediction intervals may be as high as 15 percent. Because it will not be possible to increase the number of background data in order to reduce the false-positive error rate, the Wilcoxan-Rank Sum Test will be used when the percentage of nondetects is between 50 and 90 percent. The Wilcoxan test can be used with unequal sample sizes, and so can be used for inter- or intra-point comparisons.

d) If the percentage of nondetects in the database for the sample point is 90 percent or greater, then calculate a Poisson prediction limit (see page A11-B-63).

e) If the percentage of nondetects in the background data set is 100 percent, then any operational monitoring sampling result that exceeds the RDL will require that an additional individual sample be collected and analyzed for that parameter. If the confirmatory sample result is less than the RDL, then no further action will be required. If the confirmatory sample has a reportable value, then the detection will be handled according to the procedures outlined for each media.

11B.11 Description of Media-Specific Statistical Tests for Operational Monitoring

- *Soil Monitoring*

  The soil monitoring program is detailed in Attachment 11D. The results of the annual sampling to be conducted at the six locations along the entrance road will be compared against the background data set for each parameter listed in the statistical evaluation program. If comparison of any of the operational monitoring data to background data shows a statistically significant difference and exceeds the Part 201 of Act 451 Generic Industrial Cleanup Criteria (MDNR Operational Memorandum #14, Revision 2, June 6, 1995), then the steps outlined in Subsection 11.3 will be performed.

- *Sedimentation Basin Monitoring*

  The sedimentation basin monitoring program is detailed in Attachment 11H. The results from the semiannual sampling at each of the four locations in the sedimentation basin will be evaluated on an intra-point comparison basis for each parameter listed in the statistical evaluation plan, meaning that the operational monitoring data at a sampling point will be tested against the background monitoring data set from that point. Statistical testing for new or additional parameters will begin only after the requisite background sampling has been completed and the background values have been calculated. If comparison of any of the operational monitoring data to background data shows a statistically significant difference and exceeds the Part 201 of Act 451 Generic Industrial Cleanup Criteria (MDNR Operational Memorandum #14, Revision 2, June 6, 1995), then the steps outlined in Subsection 11.8.3 will be performed.

- *Surface Water Monitoring*

  The surface water monitoring program is detailed in Attachment 11F. The results from quarterly sampling of water from Allen Drain will be evaluated on an intra-point comparison basis for each parameter listed in the statistical evaluation plan, meaning that the operational monitoring data at the sampling point will be tested against the background monitoring data set from that point. For parameters not yet measured in the drain, statistical testing will begin only after the requisite number of background samples have been analyzed and the appropriate background values have been calculated. If comparison of any of the operational monitoring data to background data results in a statistically significant difference, then the steps outlined in Subsection 11.6.3 will be performed.

- *Leak Detection System Monitoring*

  The leak detection monitoring program is detailed Attachment 11I. The results from the quarterly samples collected from the leak detection system (if sufficient volumes are available for analysis), will be evaluated on an intra-point comparison basis for each parameter listed in the statistical evaluation plan, meaning that the operational monitoring data at the sampling point will be tested against the background monitoring data set from that point. Statistical testing for new or additional parameters will begin only after the requisite number of background samples have been analyzed and the background values have been calculated. If comparison of any of the operational monitoring data to background data shows a statistically significant difference, then the steps outlined in Subsection 11.9.3 will be performed.

- *Lysimeter Monitoring*

  The lysimeter monitoring program is described in Attachment 11J. The results from the quarterly samples collected from each of the two lysimeters (if sufficient volumes are present for analysis) will be evaluated on an intra-point comparison basis for each parameter listed in the statistical evaluation plan, meaning that the operational monitoring data at the sampling point will be tested against the background monitoring data set from that point. If comparison of any of the operational monitoring data to background data shows a statistically significant difference, then the steps outlined in Subsection 11.10.3 will be performed.

11B.12 References

MDNR. 1991. MDNR Act 64 Cleanup Verification Guidance Document.

USEPA. 1989. Statistical Analysis of Ground Water Monitoring Data at RCRA Facilities - Interim Final Guidance. April 1987.

USEPA. 1993. Statistical Analysis of Ground Water Monitoring Data at RCRA Facilities - Addendum to Interim Final Guidance. February 1993.

STATISTICAL METHODS ATTACHMENT

Information Taken From:

- **USEPA. 1989. Statistical Analysis of Ground Water Monitoring Data at RCRA Facilities - Interim Final Guidance. April 1987.**

- **USEPA. 1993. Statistical Analysis of Ground Water Monitoring Data at RCRA Facilities - Interim Final Guidance. February 1993.**

STATISTICAL METHODS ATTACHMENT

PROBABILITY PLOTS

USEPA 1993

1.1.2 Probability Plots

As suggested within the Interim Final Guidance, a simple, yet useful graphical test for Normality is to plot the data on probability paper. The y-axis is scaled to represent probabilities according to the Normal distribution and the data are arranged in increasing order. An observed value is plotted on the x-axis and the proportion of observations less than or equal to each observed value is plotted as the y-coordinate. The scale is constructed so that, if the data are Normal, the points when plotted will approximate a straight line. Visually apparent curves or bends indicate that the data do not follow a Normal distribution (see Interim Final Guidance, pp. 4-8 to 4-11).

Probability Plots are particularly useful for spotting irregularities within the data when compared to a specific distributional model like the Normal. It is easy to determine whether departures from Normality are occurring more or less in the middle ranges of the data or in the extreme tails. Probability Plots can also indicate the presence of possible outlier values that do not follow the basic pattern of the data and can show the presence of significant positive or negative skewness.

If a (Normal) Probability Plot is done on the combined data from several wells and Normality is accepted, it implies that all of the data came from the same Normal distribution. Consequently, each subgroup of the data set (e.g., observations from distinct wells), has the same mean and standard deviation. If a Probability Plot is done on the data residuals (each value minus its subgroup mean) and is not a straight line, the interpretation is more complicated. In this case, either the residuals are not Normal, or there is a subgroup of the data with a Normal distribution but a different mean or standard deviation than the other subgroups. The Probability Plot will indicate a deviation from the underlying Normality assumption either way.

The same Probability Plot technique may be used to investigate whether a set of data or residuals follows the Lognormal distribution. The procedure is the same, except that one first replaces each observation by its natural logarithm. After the data have been transformed to their natural logarithms, the Probability Plot is constructed as before. The only difference is that the natural logarithms of the observations are used on the x-axis. If the data are Lognormal, the Probability Plot (on Normal probability paper) of the logarithms of the observations will approximate a straight line.

Many statistical software packages for personal computers will construct Probability Plots automatically with a simple command or two. If such software is available, there is no need to construct Probability Plots by hand or to obtain special graph paper. The plot itself may be generated somewhat differently than the method described above. In some packages, the observed value is plotted as before on the x-axis. The y-axis, however, now represents the quantile of the Normal distribution (often referred to as the "Normal score of the observation") corresponding to the cumulative probability of the observed value. The y-coordinate is often computed by the following formula:

$$y_i = \Phi^{-1}\left(\frac{i}{n+1}\right)$$

where Φ^{-1} denotes the inverse of the cumulative Normal distribution, n represents the sample size, and i represents the rank position of the ith ordered concentration. Since the computer does these calculations automatically, the formula does not have to be computed by hand.

EXAMPLE 1

Determine whether the following data set follows the Normal distribution by using a Probability Plot.

Month	Nickel Concentration (ppb) Well 1	Well 2	Well 3	Well 4
1	58.8	19	39	3.1
2	1.0	81.5	151	942
3	262	331	27	85.6
4	56	14	21.4	10
5	8.7	64.4	578	637

SOLUTION

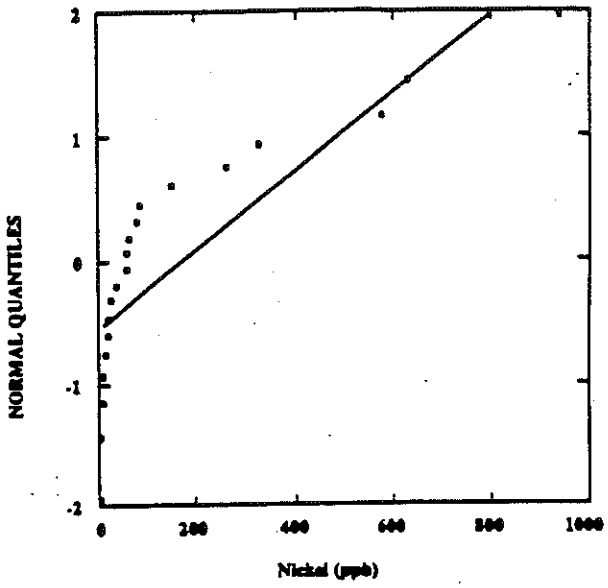
Step 1. List the measured nickel concentrations in order from lowest to highest.

Nickel Concentration (ppb)	Order (i)	Probability 100*(i/(n+1))	Normal Quantile
1	1	5	-1.645
3.1	2	10	-1.28
8.7	3	14	-1.08
10	4	19	-0.88
14	5	24	-0.706
19	6	29	-0.55
21.4	7	33	-0.44
27	8	38	-0.305
39	9	43	-0.176
56	10	48	-0.05
58.8	11	52	0.05
64.4	12	57	0.176
81.5	13	62	0.305
85.6	14	67	0.44
151	15	71	0.55
262	16	76	0.706
331	17	81	0.88
578	18	86	1.08
637	19	90	1.28
942	20	95	1.645

Step 2. The cumulative probability is given in the third column and is computed as 100*(i/(n+1)) where n is the total number of samples (n=20). The last column gives the Normal quantiles corresponding to these probabilities.

Step 3. If using special graph paper, plot the probability versus the concentration for each sample. Otherwise, plot the Normal quantile versus the concentration for each sample, as in the plot below. The curvature found in the Probability Plot indicates that there is evidence of non-Normality in the data.

PROBABILITY PLOT



USEPA, 1989

4.2.3 Plotting on Probability Paper

PURPOSE

Probability paper is a visual aid and diagnostic tool in determining whether a small set of data follows a normal distribution. Also, approximate estimates of the mean and standard deviation of the distribution can be read from the plot.

PROCEDURE

Let X be the variable; X_1, X_2,...,X_i,...,X_n the set of n observations. The values of X can be raw data, residuals, or transformed data.

Step 1. Rearrange the observations in ascending order:

$$X(1), X(2),\ldots,X(n).$$

Step 2. Compute the cumulative frequency for each distinct value X(i) as $(i/(n+1)) \times 100\%$. The divisor of (n+1) is a plotting convention to avoid cumulative frequencies of 100% which would be at infinity on the probability paper.

If a value of X occurs more than once, then the corresponding value of i increases appropriately. For example, if X(2) = X(3), then the cumulative frequency for X(1) is 100*1/(n+1), but the cumulative frequency for X(2) or X(3) is 100*(1+2)/(n+1).

Step 3. Plot the distinct pairs [X(i), (i/n+1)) x 100] values on probability paper (this paper is commercially available) using an appropriate scale for X on the horizontal axis. The vertical axis for the cumulative frequencies is already scaled from 0.01 to 99.99%.

If the points fall roughly on a straight line (the line can be drawn with a ruler), then one can conclude that the underlying distribution is approximately normal. Also, an estimate of the mean and standard deviation can be made from the plot. The horizontal line drawn through 50% cuts the plotted line at the mean of the X values. The horizontal line going through 84% cuts the line at a value corresponding to the mean plus one standard deviation. By subtraction, one obtains the standard deviation.

REFERENCE

Dixon, W. J., and F. J. Massey, Jr. *Introduction to Statistical Analysis.* McGraw-Hill, Fourth Edition, 1983.

EXAMPLE

Table 4-2 lists 22 distinct chlordane concentration values (X) along with their frequencies. These are the same values as those listed in Table 4-1. There is a total of n=24 observations.

Step 1. Sort the values of X in ascending order (column 1).

Step 2. Compute [100 x (i/25)], column 4, for each distinct value of X, based on the values of i (column 2).

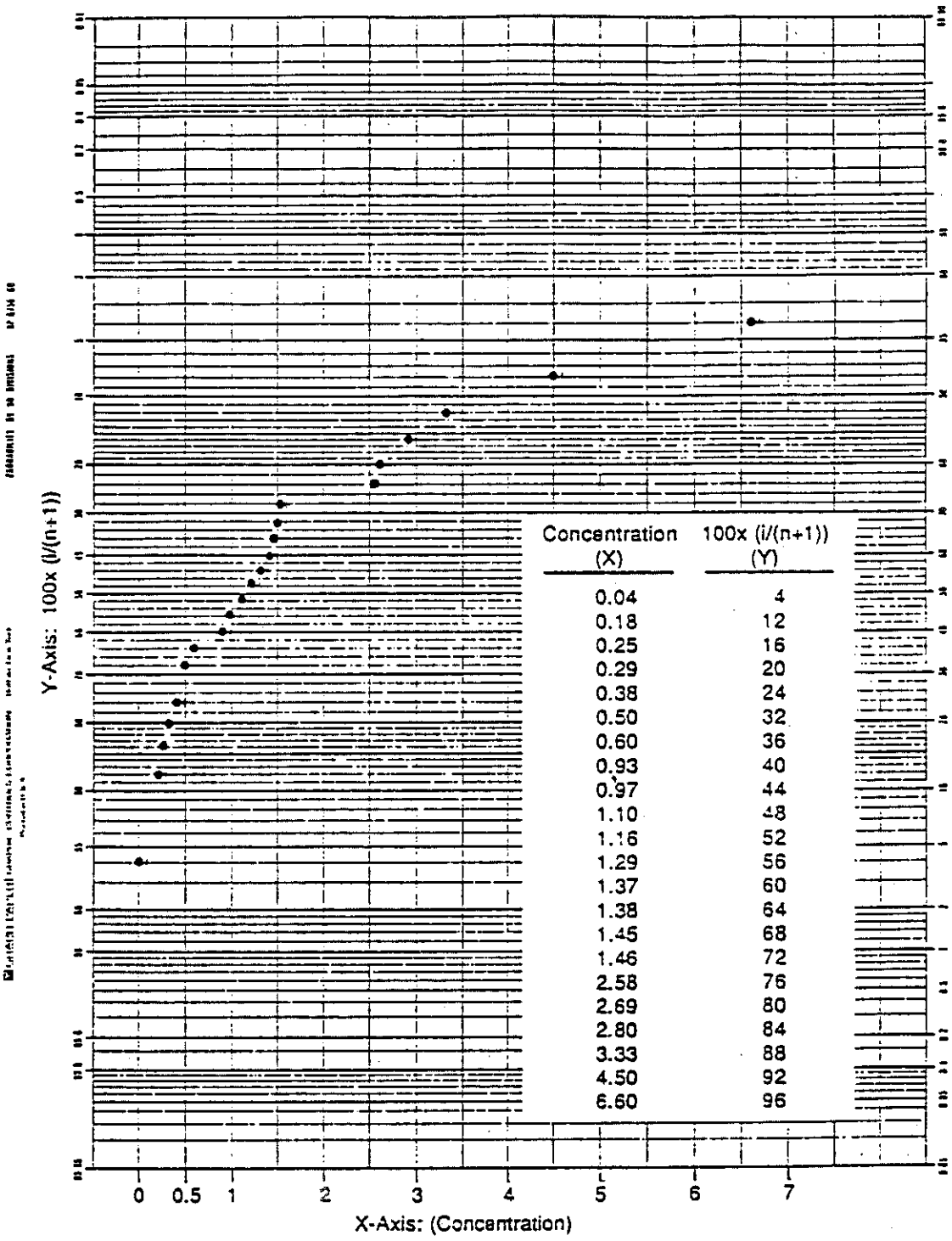
Step 3. Plot the pairs $[X_i, 100x(i/25)]$ on probability paper (Figure 4-2).

INTERPRETATION

The points in Figure 4-2 do not fall on a straight line; therefore, the hypothesis of an underlying normal distribution is rejected. However, the

TABLE 4-2. EXAMPLE DATA COMPUTATIONS FOR PROBABILITY PLOTTING

	Concentration X	Absolute frequency	i	100x(i/(n+1))	ln(X)
	0.04	1	1	4	-3.22
	0.18	2	3	12	-1.71
	0.25	1	4	16	-1.39
	0.29	1	5	20	-1.24
	0.38	1	6	24	-0.97
	0.50	2	8	32	-0.69
	0.60	1	9	36	-0.51
Dissolved phase	0.93	1	10	40	-0.07
	0.97	1	11	44	-0.03
	1.10	1	12	48	0.10
	1.16	1	13	52	0.15
	1.29	1	14	56	0.25
	1.37	1	15	60	0.31
	1.38	1	16	64	0.32
	1.45	1	17	68	0.37
----------	1.46	1	18	72	0.38
	2.58	1	19	76	0.95
	2.69	1	20	80	0.99
Immiscible phase	2.80	1	21	84	1.03
	3.33	1	22	88	1.20
	4.50	1	23	92	1.50
	6.60	1	24	96	1.89



Concentration (X)	100x (i/(n+1)) (Y)
0.04	4
0.18	12
0.25	16
0.29	20
0.38	24
0.50	32
0.60	36
0.93	40
0.97	44
1.10	48
1.16	52
1.29	56
1.37	60
1.38	64
1.45	68
1.46	72
2.58	76
2.69	80
2.80	84
3.33	88
4.50	92
6.60	96

Figure 4-2. Probability plot of raw chlordane concentrations.

shape of the curve indicates a lognormal distribution. This is checked in the next step.

Also, information about the solubility of chlordane in this example is helpful. Chlordane has a solubility (in water) that ranges between 0.0156 and 1.85 mg/L. Because the last six measurements exceed this solubility range, contamination is suspected.

Next, take the natural logarithm of the X-values (ln(X)) (column 5 in Table 4-2). Repeat Step 3 above using the pairs [ln(X), 100x(i/25)]. The resulting plot is shown in Figure 4-3. The points fall approximately on a straight line (hand-drawn) and the hypothesis of lognormality of X, i.e., ln(X) is normally distributed, can be accepted. The mean can be estimated at slightly below 0 and the standard deviation at about 1.2 on the log scale.

CAUTIONARY NOTE

The probability plot is not a formal test of whether the data follow a normal distribution. It is designed as a quick, graphical procedure to identify cases of obvious nonnormality. Figure 4-3 is an example of a probability plot of normal data, illustrating how a probability plot of normal data looks. Figure 4-2 is an example of how nonnormal data look on a probability plot. Data that are sufficiently nonnormal to require use of a procedure not based on the normal distribution will show a definite curve. A single point that does not fall on the straight line does not indicate nonnormality, but may be an outlier.

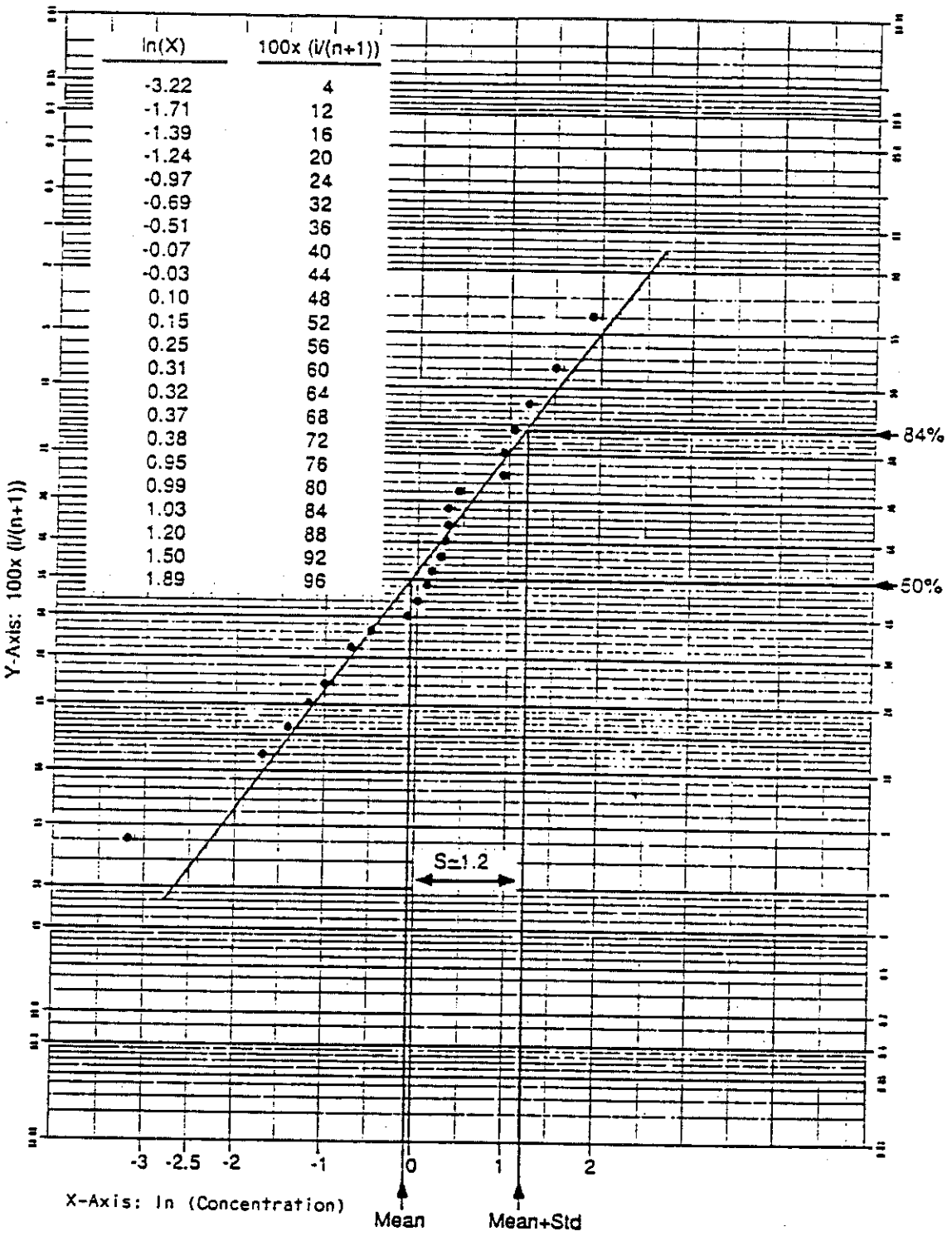


Figure 4-3. Probability plot of log-transformed chlordane concentrations.

STATISTICAL METHODS ATTACHMENT

OUTLIER TESTING

USEPA, 1993

6.2 OUTLIER TESTING

Formal testing for outliers should be done only if an observation seems particularly high (by orders of magnitude) compared to the rest of the data set. If a sample value is suspect, one should run the outlier test described on pp. 8-11 to 8-14 of the EPA guidance document. It should be cautioned, however, that this outlier test assumes that the rest of the data values, except for the suspect observation, are Normally distributed (Barnett and Lewis, 1978). Since Lognormally distributed measurements often contain one or more values that appear high relative to the rest, it is recommended that the outlier test be run on the logarithms of the data instead of the original observations. That way, one can avoid classifying a high Lognormal measurement as an outlier just because the test assumptions were violated.

If the test designates an observation as a statistical outlier, the sample should not be treated as such until a specific reason for the abnormal measurement can be determined. Valid reasons may, for example, include contaminated sampling equipment, laboratory contamination of the sample, or

errors in transcription of the data values. Once a specific reason is documented, the sample should be excluded from any further statistical analysis. If a plausible reason cannot be found, the sample should be treated as a true but extreme value, not to be excluded from further analysis.

EXAMPLE 19

The table below contains data from five wells measured over a 4-month period. The value 7066 is found in the second month at well 3. Determine whether there is statistical evidence that this observation is an outlier.

Carbon Tetrachloride Concentration (ppb)				
Well 1	Well 2	Well 3	Well 4	Well 5
1.69	302	16.2	199	275
3.25	35.1	7066	41.6	6.5
7.3	15.6	350	75.4	59.7
12.1	13.7	70.14	57.9	68.4

SOLUTION

Step 1. Take logarithms of each observation. Then order and list the logged concentrations.

Order	Concentration (ppb)	Logged Concentration
1	1.69	0.525
2	3.25	1.179
3	6.5	1.872
4	7.3	1.988
5	12.1	2.493
6	13.7	2.617
7	15.6	2.747
8	16.2	2.785
9	35.1	3.558
10	41.6	3.728
11	57.9	4.059
12	59.7	4.089
13	68.4	4.225
14	70.1	4.250
15	75.4	4.323
16	199	5.293
17	275	5.617
18	302	5.710
19	350	5.878
20	7066	8.863

Step 2. Calculate the mean and SD of all the logged measurements. In this case, the mean and SD are 3.789 and 1.916, respectively.

Step 3. Calculate the outlier test statistic T_{20} as

$$T_{20} = \frac{X_{(20)} - \overline{X}}{SD} = \frac{8.863 - 3.789}{1.916} = 2.648.$$

Step 4. Compare the observed statistic T_{20} with the critical value of 2.557 for a sample size n=20 and a significance level of 5 percent (taken from Table 8 on p. B-12 of the Interim Final Guidance). Since the observed value T_{20}=2.648 exceeds the critical value, there is significant evidence that the largest observation is a statistical outlier. Before excluding this value from further analysis, a valid explanation for this unusually high value should be found. Otherwise, treat the outlier as an extreme but valid concentration measurement.

USEPA, 1989

8.2 OUTLIERS

A ground-water constituent concentration value that is much different from most other values in a data set for the same ground-water constituent concentration can be referred to as an "outlier." Possible reasons for outliers can be:

- A catastrophic unnatural occurrence such as a spill;
- Inconsistent sampling or analytical chemistry methodology that may result in laboratory contamination or other anomalies;
- Errors in the transcription of data values or decimal points; and
- True but extreme ground-water constituent concentration measurements.

There are several tests to determine if there is statistical evidence that an observation is an outlier. The reference for the test presented here is ASTM paper E178-75.

PURPOSE

The purpose of a test for outliers is to determine whether there is statistical evidence that an observation that appears extreme does not fit the distribution of the rest of the data. If a suspect observation is identified as an outlier, then steps need to be taken to determine whether it is the result of an error or a valid extreme observation.

PROCEDURE

Let the sample of observations of a hazardous constituent of ground water be denoted by $X_1, \ldots, X_n$. For specificity, assume that the data have been ordered and that the largest observation, denoted by X_n, is suspected of being an outlier. Generally, inspection of the data suggests values that do not

appear to belong to the data set. For example, if the largest observation is an order of magnitude larger than the other observations, it would be suspect.

Step 1. Calculate the mean, $\bar{X}$ and the standard deviation, S, of the data including all observations.

Step 2. Form the statistic, T_n:

$$T_n = (X_n - \bar{X})/S$$

Note that T_n is the difference between the largest observation and the sample mean, divided by the sample standard deviation.

Step 3. Compare the statistic T_n to the critical value given the sample size, n, in Table 8 in Appendix B. If the T_n statistic exceeds the critical value from the table, this is evidence that the suspect observation, X_n, is a statistical outlier.

Step 4. If the value is identified as an outlier, one of the actions outlined below should be taken. (The appropriate action depends on what can be learned about the observation.) The records of the sampling and analysis of the sample that led to it should be investigated to determine whether the outlier resulted from an error that can be identified.

- If an error (in transcription, dilution, analytical procedure, etc.) can be identified and the correct value recovered, the observation should be replaced by its corrected value and the appropriate statistical analysis done with the corrected value.

- If it can be determined that the observation is in error, but the correct value cannot be determined, then the observation should be deleted from the data set and the appropriate statistical analysis performed. The fact that the observation was deleted and the reason for its deletion should be reported when reporting the results of the statistical analysis.

- If no error in the value can be documented then it must be assumed that the observation is a true but extreme value. In this case it must not be altered. It may be desirable to obtain another sample to confirm the observation. However, analysis and reporting should retain the observation and state that no error was found in tracing the sample that led to the extreme observation.

EXAMPLE

Table 8-4 contains 19 values of total organic carbon (TOC) that were obtained from a monitoring well. Inspection shows one value which at 11,000 mg/L is nearly an order of magnitude larger than most of the other observations. It is a suspected outlier.

TABLE 8-4. EXAMPLE DATA FOR TESTING FOR AN OUTLIER

Total organic carbon (mg/L)
1,700
1,900
1,500
1,300
11,000
1,250
1,000
1,300
1,200
1,450
1,000
1,300
1,000
2,200
4,900
3,700
1,600
2,500
1,900

Step 1. Calculate the mean and standard deviation of the data.

$$\bar{X} = 2300 \text{ and } S = 2325.9$$

Step 2. Calculate the statistic T_{19}.

$$T_{19} = (11000-2300)/2325.9 = 3.74$$

Step 3. Referring to Table 8 of Appendix B for the upper 5% significance level, with n = 19, the critical value is 2.532. Since the value of the statistic T_{19} = 3.74 is greater than 2.532, there is statistical evidence that the largest observation is an outlier.

Step 4. In this case, tracking the data revealed that the unusual value of 11,000 resulted from a keying error and that the correct value was 1,100. This correction was then made in the data.

INTERPRETATION

An observation that is 4 or 5 times as large as the rest of the data is generally viewed with suspicion. An observation that is an order of magnitude different could arise by a common error of misplacing a decimal. The test for an outlier provides a statistical basis for determining whether an observation

is statistically different from the rest of the data. If it is, then it is a statistical outlier. However, a statistical outlier may not be dropped or altered just because it has been identified as an outlier. The test provides a formal identification of an observation as an outlier, but does not identify the cause of the difference.

Whether or not a statistical test is done, any suspect data point should be checked. An observation may be corrected or dropped only if it can be determined that an error has occurred. If the error can be identified and corrected (as in transcription or keying) the correction should be made and the corrected values used. A value that is demonstrated to be incorrect may be deleted from the data. However, if no specific error can be documented, the observation must be retained in the data. Identification of an observation as an outlier but with no error documented could be used to suggest resampling to confirm the value.

TABLE 8. CRITICAL VALUES FOR T_n (ONE-SIDED TEST) WHEN THE STANDARD DEVIATION IS CALCULATED FROM THE SAME SAMPLE

Number of Observations, n	Upper 0.1% Significance Level	Upper 0.5% Significance Level	Upper 1% Significance Level	Upper 2.5% Significance Level	Upper 5% Significance Level	Upper 10% Significance Level
3	1.155	1.155	1.155	1.155	1.153	1.148
4	1.499	1.496	1.492	1.481	1.463	1.425
5	1.780	1.764	1.749	1.715	1.672	1.602
6	2.011	1.973	1.944	1.887	1.822	1.729
7	2.201	2.139	2.097	2.020	1.938	1.828
8	2.358	2.274	2.221	2.126	2.032	1.909
9	2.492	2.387	2.323	2.215	2.110	1.977
10	2.606	2.482	2.410	2.290	2.176	2.036
11	2.705	2.564	2.485	2.355	2.234	2.088
12	2.791	2.636	2.550	2.412	2.285	2.134
13	2.867	2.699	2.607	2.462	2.331	2.175
14	2.935	2.755	2.659	2.507	2.371	2.213
15	2.997	2.806	2.705	2.549	2.409	2.247
16	3.052	2.852	2.747	2.585	2.443	2.279
17	3.103	2.894	2.785	2.620	2.475	2.309
18	3.149	2.932	2.821	2.651	2.504	2.335
19	3.191	2.968	2.854	2.681	2.532	2.361
20	3.230	3.001	2.884	2.709	2.557	2.385
21	3.266	3.031	2.912	2.733	2.580	2.408
22	3.300	3.060	2.939	2.758	2.603	2.429
23	3.332	3.087	2.963	2.781	2.624	2.448
24	3.362	3.112	2.987	2.802	2.644	2.467
25	3.389	3.135	3.009	2.822	2.663	2.486
26	3.415	3.157	3.029	2.841	2.681	2.502
27	3.440	3.178	3.049	2.859	2.698	2.519
28	3.464	3.199	3.068	2.876	2.714	2.534
29	3.486	3.218	3.085	2.893	2.730	2.549
30	3.507	3.236	3.103	2.908	2.745	2.563
31	3.528	3.253	3.119	2.924	2.759	2.577
32	3.546	3.270	3.135	2.938	2.773	2.591
33	3.565	3.286	3.150	2.952	2.786	2.604
34	3.582	3.301	3.164	2.965	2.799	2.616
35	3.599	3.316	3.178	2.979	2.811	2.628
36	3.616	3.330	3.191	2.991	2.823	2.639
37	3.631	3.343	3.204	3.003	2.835	2.650
38	3.646	3.356	3.216	3.014	2.846	2.661
39	3.660	3.369	3.228	3.025	2.857	2.671
40	3.673	3.381	3.240	3.036	2.866	2.682
41	3.687	3.393	3.251	3.046	2.877	2.692
42	3.700	3.404	3.261	3.057	2.887	2.700
43	3.712	3.415	3.271	3.067	2.896	2.710
44	3.724	3.425	3.282	3.075	2.905	2.719
45	3.736	3.435	3.292	3.085	2.914	2.727
46	3.747	3.445	3.302	3.094	2.923	2.736
47	3.757	3.455	3.310	3.103	2.931	2.744
48	3.768	3.464	3.319	3.111	2.940	2.753
49	3.779	3.474	3.329	3.120	2.948	2.760
50	3.789	3.483	3.336	3.128	2.956	2.768

(Continued)

TABLE 8 (Continued)

Number of Observations, n	Upper 0.1% Significance Level	Upper 0.5% Significance Level	Upper 1% Significance Level	Upper 2.5% Significance Level	Upper 5% Significance Level	Upper 10% Significance Level
51	3.798	3.491	3.245	3.136	2.964	2.775
52	3.808	3.500	3.353	3.143	2.971	2.783
53	3.816	3.507	3.361	3.151	2.978	2.790
54	3.825	3.516	3.368	3.158	2.986	2.798
55	3.834	3.524	3.376	3.166	2.992	2.804
56	3.842	3.531	3.383	3.172	3.000	2.811
57	3.851	3.539	3.391	3.180	3.006	2.818
58	3.858	3.546	3.397	3.186	3.013	2.824
59	3.867	3.553	3.405	3.193	3.019	2.831
60	3.874	3.560	3.411	3.199	3.025	2.837
61	3.882	3.566	3.418	3.205	3.032	2.842
62	3.889	3.573	3.424	3.212	3.037	2.849
63	3.896	3.579	3.430	3.218	3.044	2.854
64	3.903	3.586	3.437	3.224	3.049	2.860
65	3.910	3.592	3.442	3.230	3.055	2.866
66	3.917	3.598	3.449	3.235	3.061	2.871
67	3.923	3.605	3.454	3.241	3.066	2.877
68	3.930	3.610	3.460	3.246	3.071	2.883
69	3.936	3.617	3.466	3.252	3.076	2.888
70	3.942	3.622	3.471	3.257	3.082	2.893
71	3.948	3.627	3.476	3.262	3.087	2.897
72	3.954	3.633	3.482	3.267	3.092	2.903
73	3.960	3.638	3.487	3.272	3.098	2.908
74	3.965	3.643	3.492	3.278	3.102	2.912
75	3.971	3.648	3.496	3.282	3.107	2.917
76	3.977	3.654	3.502	3.287	3.111	2.922
77	3.982	3.658	3.507	3.291	3.117	2.927
78	3.987	3.663	3.511	3.297	3.121	2.931
79	3.992	3.669	3.516	3.301	3.125	2.935
80	3.998	3.673	3.521	3.305	3.130	2.940
81	4.002	3.677	3.525	3.309	3.134	2.945
82	4.007	3.682	3.529	3.315	3.139	2.949
83	4.012	3.687	3.534	3.319	3.143	2.953
84	4.017	3.691	3.539	3.323	3.147	2.957
85	4.021	3.695	3.543	3.327	3.151	2.961
86	4.026	3.699	3.547	3.331	3.155	3.966
87	4.031	3.704	3.551	3.335	3.160	2.970
88	4.035	3.708	3.555	3.339	3.163	2.973
89	4.039	3.712	3.559	3.343	3.167	2.977
90	4.044	3.716	3.563	3.347	3.171	2.981
91	4.049	3.720	3.567	3.350	3.174	2.984
92	4.053	3.725	3.570	3.355	3.179	2.989
93	4.057	3.728	3.575	3.358	3.182	2.993
94	4.060	3.732	3.579	3.362	3.186	2.996
95	4.064	3.736	3.582	3.365	3.189	3.000
96	4.069	3.739	3.586	3.369	3.193	3.003
97	4.073	3.744	3.589	3.372	3.196	3.006
98	4.076	3.747	3.593	3.377	3.201	3.011
99	4.080	3.750	3.597	3.380	3.204	3.014
100	4.084	3.754	3.600	3.383	3.207	3.017

(Continued)

TABLE 8 (Continued)

Number of Observations, n	Upper 0.1% Significance Level	Upper 0.5% Significance Level	Upper 1% Significance Level	Upper 2.5% Significance Level	Upper 5% Significance Level	Upper 10% Significance Level
101	4.098	3.757	3.603	3.386	3.210	3.021
102	4.092	3.760	3.607	3.390	3.214	3.024
103	4.095	3.765	3.610	3.393	3.217	3.027
104	4.098	3.768	3.614	3.397	3.220	3.030
105	4.102	3.771	3.617	3.400	3.224	3.033
106	4.105	3.774	3.620	3.403	3.227	3.037
107	4.109	3.777	3.623	3.406	3.230	3.040
108	4.112	3.780	3.626	3.409	3.233	3.043
109	4.116	3.784	3.629	3.412	3.236	3.046
110	4.119	3.787	3.632	3.415	3.239	3.049
111	4.122	3.790	3.636	3.418	3.242	3.052
112	4.125	3.793	3.639	3.422	3.245	3.055
113	4.129	3.796	3.642	3.424	3.248	3.058
114	4.132	3.799	3.645	3.427	3.251	3.061
115	4.135	3.802	3.647	3.430	3.254	3.064
116	4.138	3.805	3.650	3.433	3.257	3.067
117	4.141	3.808	3.653	3.435	3.259	3.070
118	4.144	3.811	3.656	3.438	3.262	3.073
119	4.146	3.814	3.659	3.441	3.265	3.075
120	4.150	3.817	3.662	3.444	3.267	3.078
121	4.153	3.819	3.665	3.447	3.270	3.081
122	4.156	3.822	3.667	3.450	3.274	3.083
123	4.159	3.824	3.670	3.452	3.276	3.086
124	4.161	3.827	3.672	3.455	3.279	3.089
125	4.164	3.831	3.675	3.457	3.281	3.092
126	4.166	3.833	3.677	3.460	3.284	3.095
127	4.169	3.836	3.680	3.462	3.286	3.097
128	4.173	3.838	3.683	3.465	3.289	3.100
129	4.175	3.840	3.686	3.467	3.291	3.102
130	4.178	3.843	3.688	3.470	3.294	3.104
131	4.180	3.845	3.690	3.473	3.296	3.107
132	4.183	3.848	3.693	3.475	3.298	3.109
133	4.185	3.850	3.695	3.478	3.302	3.112
134	4.188	3.853	3.697	3.480	3.304	3.114
135	4.190	3.856	3.700	3.482	3.306	3.116
136	4.193	3.858	3.702	3.484	3.309	3.119
137	4.196	3.860	3.704	3.487	3.311	3.122
138	4.198	3.863	3.707	3.489	3.313	3.124
139	4.200	3.865	3.710	3.491	3.315	3.126
140	4.203	3.867	3.712	3.493	3.318	3.129
141	4.205	3.869	3.714	3.497	3.320	3.131
142	4.207	3.871	3.716	3.499	3.322	3.133
143	4.209	3.874	3.719	3.501	3.324	3.135
144	4.212	3.876	3.721	3.503	3.326	3.138
145	4.214	3.879	3.723	3.505	3.328	3.140
146	4.216	3.881	3.725	3.507	3.331	3.142
147	4.219	3.883	3.727	3.509	3.334	3.144

SOURCE: ASTM Designation E178-75, 1975. "Standard Recommended Practice for Dealing With Outlying Observations."

STATISTICAL METHODS ATTACHMENT

PREDICTION INTERVALS

USEPA, 1993

4.2 PREDICTION INTERVALS

When comparing background data to compliance point samples, a Prediction interval can be constructed on the background values. If the distributions of background and compliance point data are really the same, all the compliance point samples should be contained below the upper Prediction interval limit. Evidence of contamination is indicated if one or more of the compliance samples lies above the upper Prediction limit.

With intrawell comparisons, a Prediction interval can be computed on past data to contain a specified number of future observations from the same well, provided the well has not been previously contaminated. If any one or more of the future samples falls above the upper Prediction limit, there is evidence of recent contamination at the well. The steps to calculate parametric Prediction intervals are given on pp. 5-24 to 5-28 of the Interim Final Guidance.

EXAMPLE 16

The data in the table below are benzene concentrations measured at a groundwater monitoring facility. Calculate the Prediction interval and determine whether there is evidence of contamination.

Background Well Data		Compliance Well Data	
Sampling Date	Benzene Concentration (ppb)	Sampling Date	Benzene Concentration (ppb)
Month 1	12.6	Month 4	48.0
	30.8		30.3
	52.0		42.5
	28.1		15.0
Month 2	33.3		
	44.0		n=4
	3.0		Mean=33.95
	12.8		SD=14.64

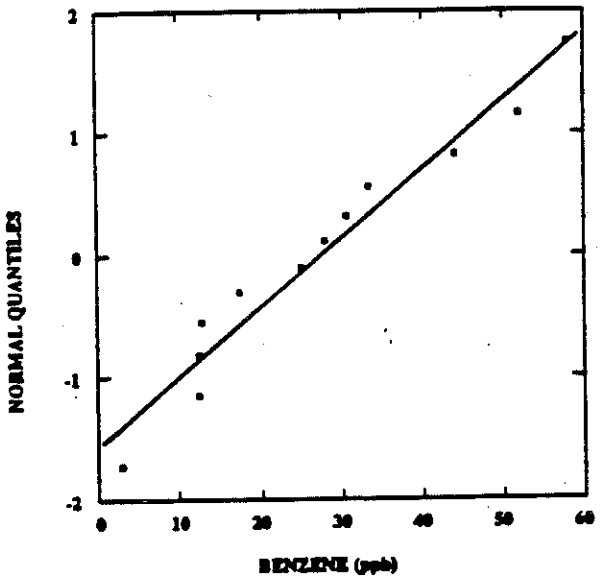
Month 3	58.1 12.6 17.6 25.3	Month 5	47.6 3.8 2.6 51.9
	n=12 Mean=27.52 SD=17.10		n=4 Mean=26.48 SD=26.94

SOLUTION

Step 1. First test the background data for approximate Normality. Only the background data are included since these values are used to construct the Prediction interval.

Step 2. A Probability Plot of the 12 background values is given below. The plot indicates an overall pattern that is reasonably linear with some modest departures from Normality. To further test the assumption of Normality, run the Shapiro-Wilk test on the background data.

PROBABILITY PLOT



Step 3. List the data in ascending and descending order as in the following table. Also calculate the differences $x_{(n-i+1)}-x_{(i)}$ and multiply by the coefficients a_{n-i+1} taken from Table A-1 to get the components of vector b_i used to calculate the Shapiro-Wilk statistic (W).

i	$x_{(i)}$	$x_{(n-i+1)}$	a_{n-i+1}	b_i
1	3.0	58.1	0.548	30.167
2	12.6	52.0	0.333	13.101
3	12.6	44.0	0.235	7.370
4	12.8	33.3	0.159	3.251
5	17.6	30.8	0.092	1.217
6	25.3	28.1	0.030	0.085
7	28.1	25.3		b=55.191
8	30.8	17.6		
9	33.3	12.8		
10	44.0	12.6		
11	52.0	12.6		
12	58.1	3.0		

Step 4. Sum the components b_i in column 5 to get quantity b. Compute the standard deviation of the background benzene values. Then the Shapiro-Wilk statistic is given as

$$W = \left[\frac{b}{SD\sqrt{n-1}}\right]^2 = \left[\frac{55.191}{17.101\sqrt{11}}\right]^2 = 0.947.$$

Step 5. The critical value at the 5% level for the Shapiro-Wilk test on 12 observations is 0.859. Since the calculated value of W=0.947 is well above the critical value, there is no evidence to reject the assumption of Normality.

Step 6. Compute the Prediction interval using the original background data. The mean and standard deviation of the 12 background samples are given by 27.52 ppb and 17.10 ppb, respectively.

Step 7. Since there are two future months of compliance data to be compared to the Prediction limit, the number of future sampling periods is k=2. At each sampling period, a mean of four independent samples will be computed, so m=4 in the prediction interval formula (see Interim Final Guidance, p. 5-25). The Bonferroni t-statistic, $t_{(11,2,.95)}$, with k=2 and 11 df is equivalent to the usual t-statistic at the .975 level with 11 df, i.e., $t_{11,.975}=2.201$.

Step 8. Compute the upper one-sided Prediction limit (UL) using the formula:

$$\bar{X} + t_{(n-1,k,.95)} S\sqrt{\frac{1}{m}+\frac{1}{n}}$$

Then the UL is given by:

$$UL = 27.52 + (17.10)(2.201)\sqrt{\frac{1}{4}+\frac{1}{12}} = 49.25 \text{ ppb}.$$

Step 9. Compare the UL to the compliance data. The means of the four compliance well observations for months 4 and 5 are 33.95 ppb and 26.48 ppb, respectively. Since the mean concentrations for months 4 and 5 are below the upper Prediction limit, there is no evidence of recent contamination at the monitoring facility.

USEPA, 1989

5.4 PREDICTION INTERVALS

A prediction interval is a statistical interval calculated to include one or more future observations from the same population with a specified confidence. This approach is algebraically equivalent to the average replicate (AR) test that is presented in the Technical Enforcement Guidance Document (TEGD), September 1986. In ground-water monitoring, a prediction interval approach may be used to make comparisons between background and compliance well data. This method of analysis is similar to that for calculating a tolerance limit, and familiarity with prediction intervals or personal preference would be the only reason for selecting them over the method for tolerance limits. The concentrations of a hazardous constituent in the background wells are used to establish an interval within which K future observations from the same population are expected to lie with a specified confidence. Then each of K future observations of compliance well concentrations is compared to the prediction interval. The interval is constructed to contain all of K future observations with the stated confidence. If any future observation exceeds the prediction interval, this is statistically significant evidence of contamination. In application, the number of future observations to be collected, K, must be specified. Thus, the prediction interval is constructed for a specified time period in the future. One year is suggested. The interval can be constructed either to contain all K individual observations with a specified probability, or to contain the K' means observed at the K' sampling periods.

The prediction interval presented here is constructed assuming that the background data all follow the same normal distribution. If that is not the case (see Section 4.2 for tests of normality), but a log transformation results in data that are adequately normal on the log scale, then the interval may still be used. In this case, use the data after transforming by taking the logarithm. The future observations need to also be transformed by taking logarithms before comparison to the interval. (Alternatively, the end points of the interval could be converted back to the original scale by taking their anti-logarithms.)

PURPOSE

The prediction interval is constructed so that K future compliance well observations can be tested by determining whether they lie in the interval or

not. If not, evidence of contamination is found. Note that the number of future observations, K, for which the interval is to be used, must be specified in advance. In practice, an owner or operator would need to construct the prediction interval on a periodic (at least yearly) basis, using the most recent background data. The interval is described using the 95% confidence factor appropriate for individual well comparisons. It is recommended that a one-sided prediction interval be constructed for the mean of the four observations from each compliance well at each sampling period.

PROCEDURE

Step 1. Calculate the mean, $\bar{X}$, and the standard deviation, S, for the background well data (used to form the prediction interval).

Step 2. Specify the number of future observations for a compliance well to be included in the interval, K. Then the interval is given by

$$[0, \bar{X} + S\sqrt{1/m + 1/n} \quad t_{(n-1,\ K,\ 0.95)}]$$

where it is assumed that the mean of the m observations taken at the K sampling periods will be used. Here n is the number of observations in the background data, and $t_{(n-1,\ K,\ 0.95)}$ is found from Table 3 in Appendix B. The table is entered with K as the number of future observations, and degrees of freedom, $\nu = n-1$. If $K > 5$, use the column for $K = 5$.

Step 3. Once the interval has been calculated, at each sampling period, the mean of the m compliance well observations is obtained. This mean is compared to see if it falls in the interval. If it does, this is reported and monitoring continues. If a mean concentration at a sampling period does not fall in the prediction interval, this is statistically significant evidence of contamination. This is also reported and the appropriate action taken.

REMARK

For a single future observation, t is given by the t-distribution found in Table 6 of Appendix B. In general, the interval to contain K future means of sample size m each is given by

$$[0, \bar{X} + S\sqrt{1/m + 1/n} \quad t_{(n-1,\ K,\ 0.95)}]$$

where t is as before from Table 3 of Appendix B and where m is the number of observations in each mean. Note that for K single observations, m=1, while for the mean of four samples from a compliance well, m=4.

Note, too, that the prediction intervals are one-sided, giving a value that should not be exceeded by the future observations. The 5% experimentwise significance level is used with the Bonferroni approach. However, to ensure

that the significance level for the individual comparisons does not go below 1%, α/K is restricted to be 1% or larger. If more than K comparisons are used, the comparisonwise significance level of 1% is used, implying that the comparisonwise level may exceed 5%.

EXAMPLE

Table 5-6 contains chlordane concentrations measured at a hypothetical facility. Twenty-four background observations are available and are used to develop the prediction interval. The prediction interval is applied to K=2 sampling periods with m=4 observations at a single compliance well each.

Step 1. Find the mean and standard deviation of the 24 background well measurements. These are 101 and 11, respectively.

Step 2. There are K = 2 future observations of means of 4 observations to be included in the prediction interval. Entering Table 3 of Appendix B at K = 2 and 20 degrees of freedom (the nearest entry to the 23 degrees of freedom), we find $t_{(20,\ 2,\ 0.95)} = 2.09$. The interval is given by

$$[0,\ 101 + (11)2.09(1/4 + 1/24)^{1/2}] = (0,\ 113.4).$$

Step 3. The mean of each of the four compliance well observations at sampling period one and two is found and compared with the interval found in Step 2. The mean of the first sampling period is 122 and that for the second sampling period is 113. Comparing the first of these to the prediction interval for two means based on samples of size 4, we find that the mean exceeds the upper limit of the prediction interval. This is statistically significant evidence of contamination and should be reported to the Regional Administrator. Since the second sampling period mean is within the prediction interval, the Regional Administrator may allow the facility to remain in its current stage of monitoring.

INTERPRETATION

A prediction interval is a statistical interval constructed from background sample data to contain a specified number of future observations from the same distribution with specified probability. That is, the prediction interval is constructed so as to have a 95% probability of containing the next K sampling period means, provided that there is no contamination. If the future observations are found to be in the prediction interval, this is evidence that there has been no change at the facility and that no contamination is occurring. If the future observation falls outside of the prediction interval, this is statistical evidence that the new observation does not come from the same distribution, that is, from the population of uncontaminated water samples previously sampled. Consequently, if the observation is a concentration above the prediction interval's upper limit, it is statistically significant evidence of contamination.

TABLE 5-6. EXAMPLE DATA FOR PREDICTION INTERVAL--CHLORDANE LEVELS

Background well data--Well 1		Compliance well data--Well 2	
Sampling date	Chlordane concentration (ppb)	Sampling date	Chlordane concentration (ppb)
January 1, 1985	97	July 1, 1986	123
	103		120
	104		116
	85		128
April 1, 1985	120	m =	4
	105	Mean =	122
	104	SD =	5
	108		
July 1, 1985	110	October 1, 1986	116
	95		117
	102		119
	78		101
October 1, 1985	105	m =	4
	94	Mean =	113
	110	SD =	8
	111		
January 1, 1986	80		
	106		
	115		
	105		
April 1, 1986	100		
	93		
	89		
	113		
n =	24		
Mean =	101		
SD =	11		

The prediction interval could be constructed in several ways. It can be developed for means of observations at each sampling period, or for each individual observation at each sampling period.

It should also be noted that the estimate of the standard deviation, S, that is used should be an unbiased estimator. The usual estimator, presented above, assumes that there is only one source of variation. If there are other sources of variation, such as time effects, or spatial variation in the data used for the background, these should be included in the estimate of the variability. This can be accomplished by use of an appropriate analysis-of-variance model to include the other factors affecting the variability. Determination of the components of variance in complicated models is beyond the scope of this document and requires consultation with a professional statistician.

REFERENCE

Hahn, G. and Wayne Nelson. 1973. "A Survey of Prediction Intervals and Their Applications." *Journal of Quality Technology*. 5:178-188.

TABLE 3. 95th PERCENTILES OF THE BONFERRONI t-STATISTICS, $t(\nu, \alpha/m)$

where ν = degrees of freedom associated with the mean squares error
m = number of comparisons
α = 0.05, the experimentwise error level

ν \ m, α/m	1 0.05	2 0.025	3 0.0167	4 0.0125	5 0.01
4	2.13	2.78	3.20	3.51	3.75
5	2.02	2.57	2.90	3.17	3.37
6	1.94	2.45	2.74	2.97	3.14
7	1.90	2.37	2.63	2.83	3.00
8	1.86	2.31	2.55	2.74	2.90
9	1.83	2.26	2.50	2.67	2.82
10	1.01	2.23	2.45	2.61	2.76
15	1.75	2.13	2.32	2.47	2.60
20	1.73	2.09	2.27	2.40	2.53
30	1.70	2.04	2.21	2.34	2.46
∞	1.65	1.96	2.13	2.24	2.33

SOURCE: For α/m = 0.05, 0.025, and 0.01, the percentiles were extracted from the t-table (Table 6, Appendix B) for values of $F=1-\alpha$ of 0.95, 0.975, and 0.99, respectively.

For α/m = 0.05/3 and 0.05/4, the percentiles were estimated using "A Nomograph of Student's t" by Nelson, L. S. 1975. *Journal of Quality Technology*, Vol. 7, pp. 200-201.

TABLE 6. PERCENTILES OF STUDENT's t-DISTRIBUTION

(F = 1-α; n = degrees of freedom)

n \ F	.60	.75	.90	.95	.975	.99	.995	.9995
1	.325	1.000	3.078	6.314	12.706	31.821	63.657	636.619
2	.289	.816	1.886	2.920	4.303	6.965	9.925	31.598
3	.277	.765	1.638	2.353	3.182	4.541	5.841	12.941
4	.271	.741	1.533	2.132	2.776	3.747	4.604	8.610
5	.267	.727	1.476	2.015	2.571	3.365	4.032	6.859
6	.265	.718	1.440	1.943	2.447	3.143	3.707	5.959
7	.263	.711	1.415	1.895	2.365	2.998	3.499	5.405
8	.262	.706	2.397	1.860	2.306	2.896	3.355	5.041
9	.261	.703	1.383	1.833	2.262	2.821	3.250	4.781
10	.260	.700	1.372	1.812	2.228	2.764	3.169	4.587
11	.260	.697	1.363	1.796	2.201	2.718	3.106	4.437
12	.259	.695	1.356	1.782	2.179	2.681	3.055	4.318
13	.259	.694	1.350	1.771	2.160	2.650	3.012	4.221
14	.258	.692	1.345	1.761	2.145	2.624	2.977	4.140
15	.258	.691	1.341	1.753	2.131	2.602	2.947	4.073
16	.258	.690	1.337	1.746	2.120	2.583	2.921	4.015
17	.257	.689	1.333	1.740	2.110	2.567	2.898	3.965
18	.257	.688	1.330	1.734	2.101	2.552	2.878	3.922
19	.257	.688	1.328	1.729	2.093	2.539	2.861	3.883
20	.257	.687	1.325	1.725	2.086	2.528	2.845	3.850
21	.257	.686	1.323	1.721	2.080	2.518	2.831	3.819
22	.256	.686	1.321	1.717	2.074	2.508	2.819	3.792
23	.256	.685	1.319	1.714	2.069	2.500	2.807	3.767
24	.256	.685	1.318	1.711	2.064	2.492	2.797	3.745
25	.256	.684	1.316	1.708	2.060	2.485	2.787	3.725
26	.256	.684	1.315	1.706	2.056	2.479	2.779	3.707
27	.256	.684	1.314	1.703	2.052	2.473	2.771	3.690
28	.256	.683	1.313	1.701	2.048	2.467	2.763	3.674
29	.256	.683	1.311	1.699	2.045	2.462	2.756	3.659
30	.256	.683	1.310	1.697	2.042	2.457	2.750	3.646
40	.255	.681	1.303	1.684	2.021	2.423	2.704	3.551
60	.254	.679	1.296	1.671	2.000	2.390	2.660	3.460
120	.254	.677	1.289	1.658	1.980	2.358	2.617	3.373
∞	.253	.674	1.282	1.645	1.960	2.326	2.576	3.291

SOURCE: *CRC Handbook of Tables for Probability and Statistics*. 1966. W. H. Beyer, Editor. Published by the Chemical Rubber Company. Cleveland, Ohio.

STATISTICAL METHODS ATTACHMENT

NONDETECTS IN STATISTICAL INTERVALS

USEPA, 1993

2.2 NONDETECTS IN STATISTICAL INTERVALS

If the chosen method is a statistical interval (Confidence, Tolerance or Prediction limit) used to compare background data against each downgradient well separately, more options are available for handling moderate proportions of nondetects. The basis of any parametric statistical interval limit is the formula $\bar{x} \pm \kappa \cdot s$, where $\bar{x}$ and s represent the sample mean and standard deviation of the (background) data and κ depends on the interval type and characteristics of the monitoring network. To use a parametric interval in the presence of a substantial number of nondetects, it is necessary to estimate the sample mean and standard deviation. But since nondetect concentrations are unknown, simple formulas for the mean and standard deviation cannot be computed directly. Two basic approaches to estimating or "adjusting" the mean and standard deviation in this situation have been described by Cohen (1959) and Aitchison (1955).

The underlying assumptions of these procedures are somewhat different. Cohen's adjustment (which is described in detail on pp. 8-7 to 8-11 of the Interim Final Guidance) assumes

that all the data (detects and nondetects) come from the same Normal or Lognormal population, but that nondetect values have been "censored" at their detection limits. This implies that the contaminant of concern is present in nondetect samples, but the analytical equipment is not sensitive to concentrations lower than the detection limit. Aitchison's adjustment, on the other hand, is constructed on the assumption that nondetect samples are free of contamination, so that all nondetects may be regarded as zero concentrations. In some situations, particularly when the analyte of concern has been detected infrequently in background measurements, this assumption may be practical, even if it cannot be verified directly.

Before choosing between Cohen's and Aitchison's approaches, it should be cautioned that Cohen's adjustment may not give valid results if the proportion of nondetects exceeds 50%. In a case study by McNichols and Davis (1988), the false positive rate associated with the use of t-tests based on Cohen's method rose substantially when the fraction of nondetects was greater than 50%. This occurred because the adjusted estimates of the mean and standard deviation are more highly correlated as the percentage of nondetects increases, leading to less reliable statistical tests (including statistical interval tests).

On the other hand, with less than 50% nondetects, Cohen's method performed adequately in the McNichols and Davis case study, provided the data were not overly skewed and that more extensive tables than those included within the Interim Final Guidance were available to calculate Cohen's adjustment parameter. As a remedy to the latter caveat, a more extensive table of Cohen's adjustment parameter is provided in Appendix A (Table A-5). It is also recommended that the data (detected measurements and nondetect detection limits) first be log-transformed prior to computing either Cohen's or Aitchison's adjustment, especially since both procedures assume that the underlying data are Normally distributed.

2.2.1 Censored and Detects-Only Probability Plots

To decide which approach is more appropriate for a particular set of ground water data, two separate Probability Plots can be constructed. The first is called a Censored Probability Plot and is a test of Cohen's underlying assumption. In this method, the combined set of detects and nondetects is ordered (with nondetects being given arbitrary but distinct ranks). Cumulative probabilities or Normal quantiles (see Section 1.1) are then computed for the data set as in a regular Probability Plot. However, only the detected values and their associated Normal quantiles are actually plotted. If the shape of the Censored Probability Plot is reasonably linear, then Cohen's assumption that nondetects have been "censored" at their detection limit is probably

acceptable and Cohen's adjustment can be made to estimate the sample mean and standard deviation. If the Censored Probability Plot has significant bends and curves, particularly in one or both tails, one might consider Aitchison's procedure instead.

To test the assumptions of Aitchison's method, a Detects-Only Probability Plot may be constructed. In this case, nondetects are completely ignored and a standard Probability Plot is constructed using only the detected measurements. Thus, cumulative probabilities or Normal quantiles are computed only for the ordered detected values. Comparison of a Detects-Only Probability Plot with a Censored Probability Plot will indicate that the same number of points and concentration values are plotted on each graph. However, different Normal quantiles are associated with each detected concentration. If the Detects-Only Probability Plot is reasonably linear, then the assumptions underlying Aitchison's adjustment (i.e., that "nondetects" represent zero concentrations, and that detects and nondetects follow separate probability distributions) are probably reasonable.

If it is not clear which of the Censored or Detects-Only Probability Plots is more linear, Probability Plot Correlation Coefficients can be computed for both approaches (note that the correlations should only involve the points actually plotted, that is, detected concentrations). The plot with the higher correlation coefficient will represent the most linear trend. Be careful, however, to use other, non-statistical judgments to help decide which of Cohen's and Aitchison's underlying assumptions appears to be most reasonable based on the specific characteristics of the data set. It is also likely that these Probability Plots may have to be constructed on the logarithms of the data instead of the original values, if in fact the most appropriate underlying distribution is the Lognormal instead of the Normal.

EXAMPLE 8

Create Censored and Detects-Only Probability Plots with the following zinc data to determine whether Cohen's adjustment or Aitchison's adjustment is most appropriate for estimating the true mean and standard deviation.

	Zinc Concentrations (ppb) at Background Wells				
Sample	Well 1	Well 2	Well 3	Well 4	Well 5
1	<7	<7	<7	11.69	<7
2	11.41	<7	12.85	10.90	<7
3	<7	13.70	14.20	<7	<7
4	<7	11.56	9.36	12.22	11.15
5	<7	<7	<7	11.05	13.31
6	10.00	<7	12.00	<7	12.35
7	15.00	10.50	<7	13.24	<7
8	<7	12.59	<7	<7	8.74

SOLUTION

Step 1. Pool together the data from the five background wells and list in order in the table below.

Step 2. To construct the Censored Probability Plot, compute the probabilities i/(n+1) using the combined set of detects and nondetects, as in column 3. Find the Normal quantiles associated with these probabilities by applying the inverse standard Normal transformation, Φ^{-1}.

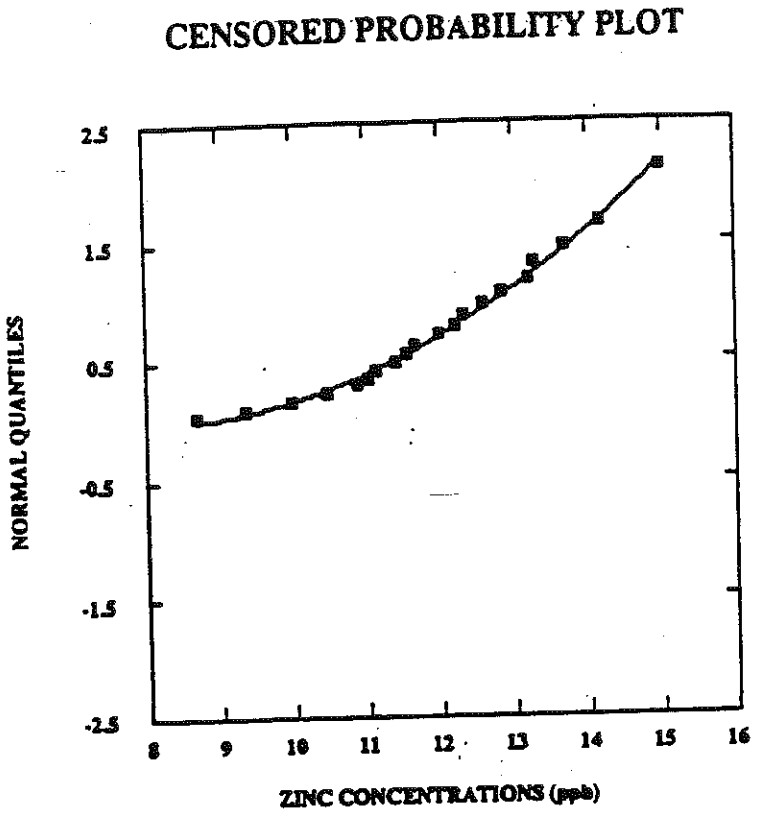
Step 3. To construct the Detects-Only Probability Plot, compute the probabilities in column 5 using only the detected zinc values. Again apply the inverse standard Normal transformation to find the associated Normal quantiles in column 6. Note that nondetects are ignored completely in this method.

Order (i)	Zinc Conc. (ppb)	Censored Probs.	Normal Quantiles	Detects-Only Probs.	Normal Quantiles
1	<7	.024	-1.971		
2	<7	.049	-1.657		
3	<7	.073	-1.453		
4	<7	.098	-1.296		
5	<7	.122	-1.165		
6	<7	.146	-1.052		
7	<7	.171	-0.951		
8	<7	.195	-0.859		
9	<7	.220	-0.774		
10	<7	.244	-0.694		
11	<7	.268	-0.618		
12	<7	.293	-0.546		
13	<7	.317	-0.476		
14	<7	.341	-0.408		
15	<7	.366	-0.343		
16	<7	.390	-0.279		
17	<7	.415	-0.216		
18	<7	.439	-0.153		
19	<7	.463	-0.092		
20	<7	.488	-0.031		
21	8.74	.512	0.031	.048	-1.668
22	9.36	.537	0.092	.095	-1.309
23	10.00	.561	0.153	.143	-1.068
24	10.50	.585	0.216	.190	-0.876
25	10.90	.610	0.279	.238	-0.712
26	11.05	.634	0.343	.286	-0.566
27	11.15	.659	0.408	.333	-0.431
28	11.41	.683	0.476	.381	-0.303
29	11.56	.707	0.546	.429	-0.180
30	11.69	.732	0.618	.476	-0.060
31	12.00	.756	0.694	.524	0.060
32	12.22	.780	0.774	.571	0.180
33	12.35	.805	0.859	.619	0.303
34	12.59	.829	0.951	.667	0.431
35	12.85	.854	1.052	.714	0.566
36	13.24	.878	1.165	.762	0.712
37	13.31	.902	1.296	.810	0.876
38	13.70	.927	1.453	.857	1.068
39	14.20	.951	1.657	.905	1.309
40	15.00	.976	1.971	.952	1.668

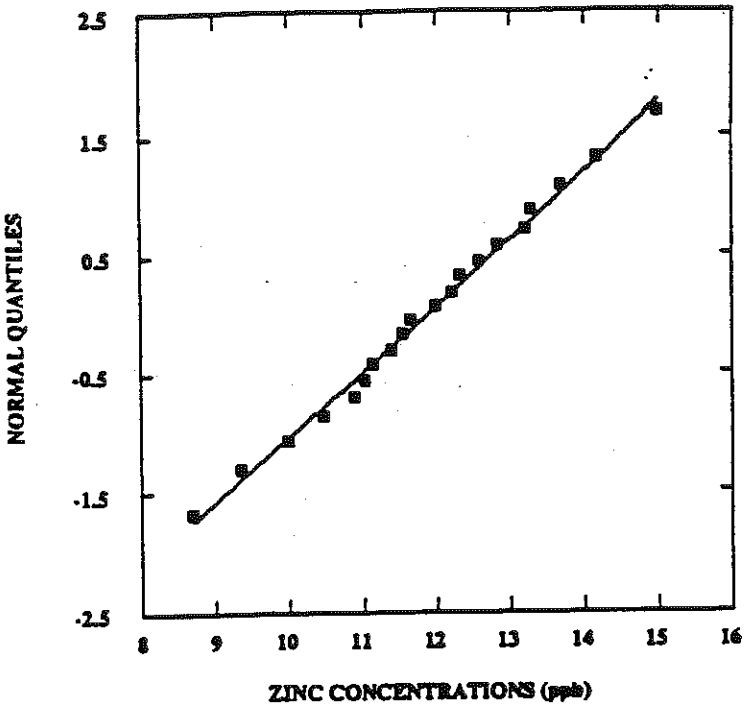
Step 4. Plot the detected zinc concentrations versus each set of probabilities or Normal quantiles, as per the procedure for constructing Probability Plots (see figures below). The nondetect values should not be plotted. As can be seen from the graphs, the Censored Probability Plot indicates a definite curvature in the tails, especially the lower tail. The Detects-Only Probability Plot, however, is reasonably linear. This visual impression is bolstered by calculation of a Probability Plot Correlation Coefficient for each set of

detected values: the Censored Probability Plot has a correlation of r=.969, while the Detects-Only Probability Plot has a correlation of r=.998.

Step 5. Because the Detects-Only Probability Plot is substantially more linear than the Censored Probability Plot, it may be appropriate to consider detects and nondetects as arising from statistically distinct distributions, with nondetects representing "zero" concentrations. Therefore, Aitchison's adjustment may lead to better estimates of the true mean and standard deviation than Cohen's adjustment for censored data.



DETECTS-ONLY PROBABILITY PLOT



2.2.2 Aitchison's Adjustment

To actually compute Aitchison's adjustment (Aitchison, 1955), it is assumed that the detected samples follow an underlying Normal distribution. If the detects are Lognormal, compute Aitchison's adjustment on the logarithms of the data instead. Let d=# nondetects and let n=total # of samples (detects and nondetects combined). Then if $\bar{x}^*$ and s^* denote respectively the sample mean and standard deviation of the detected values, the adjusted overall mean can be estimated as

$$\hat{\mu} = \left(1 - \frac{d}{n}\right)\bar{x}^*$$

and the adjusted overall standard deviation may be estimated as the square root of the quantity

$$\hat{\sigma}^2 = \frac{n-(d+1)}{n-1}(s^*)^2 + \frac{d}{n}\left(\frac{n-d}{n-1}\right)(\bar{x}^*)^2$$

The general formula for a parametric statistical interval adjusted for nondetects by Aitchison's method is given by $\hat{\mu} \pm \kappa \cdot \hat{\sigma}$, with κ depending on the type of interval being constructed.

EXAMPLE 9

In Example 8, it was determined that Aitchison's adjustment might lead to more appropriate estimates of the true mean and standard deviation than Cohen's adjustment. Use the data in Example 8 to compute Aitchison's adjustment.

SOLUTION

Step 1. The zinc data consists of 20 nondetects and 20 detected values; therefore d=20 and n=40 in the above formulas.

Step 2. Compute the average $\bar{x}^* = 11.891$ and the standard deviation $s^* = 1.595$ of the set of detected values.

Step 3. Use the formulas for Aitchison's adjustment to compute estimates of the true mean and standard deviation:

$$\hat{\mu} = \left(1 - \frac{20}{40}\right) \times 11.891 = 5.95$$

$$\hat{\sigma}^2 = \left(\frac{40-21}{39}\right)(1.595)^2 + \left(\frac{20}{40}\right)\left(\frac{20}{39}\right)(11.891)^2 = 37.495 \Rightarrow \hat{\sigma} = 6.12$$

If Cohen's adjustment is mistakenly computed on these data instead, with a detection limit of 7 ppb,the estimates become $\hat{\mu} = 7.63$ and $\hat{\sigma} = 4.83$. Thus, the choice of adjustment can have a significant impact on the upper limits computed for statistical intervals.

USEPA, 1989

8.1.3 Cohen's Method

If a confidence interval or a tolerance interval based upon the normal distribution is being constructed, a technique presented by Cohen (1959) specifies a method to adjust the sample mean and sample standard deviation to account for data below the detection limit. The only requirements for the use of this technique is that the data are normally distributed and that the detection limit be always the same. This technique is demonstrated below.

PURPOSE

Cohen's method provides estimates of the sample mean and standard deviation when some ($\leq$ 50%) observations are below detection. These estimates can then be used to construct tolerance, confidence, or prediction intervals.

PROCEDURE

Let n be the total number of observations, m represent the number of data points above the detection limit (DL), and X_i represent the value of the ith constituent value above the detection limit.

Step 1. Compute the sample mean $\bar{x}_d$ from the data above the detection limit as follows:

$$\bar{x}_d = \frac{1}{m} \sum_{i=1}^{m} x_i$$

Step 2. Compute the sample variance S_d^2 from the data above the detection limit as follows:

$$S_d^2 = \frac{\sum_{i=1}^{m} (x_i - \bar{x})^2}{m-1} = \frac{\sum_{i=1}^{m} x_i^2 - \frac{1}{m} \left(\sum_{i=1}^{m} x_i \right)^2}{m-1}$$

Step 3. Compute the two parameters, h and γ (lowercase gamma), as follows:

$$h = \frac{(n-m)}{n}$$

and

$$\gamma = \frac{S_d^2}{(\bar{x}-DL)^2}$$

where n is the total number of observations (i.e., above and below the detection limit), and where DL is equal to the detection limit.

These values are then used to determine the value of the parameter $\hat{\lambda}$ from Table 7 in Appendix B.

Step 4. Estimate the corrected sample mean, which accounts for the data below detection limit, as follows:

$$\bar{X} = \bar{x}_d - \hat{\lambda}(\bar{x}_d - DL)$$

Step 5. Estimate the corrected sample standard deviation, which accounts for the data below detection limit, as follows:

$$S = (S_d^2 + \hat{\lambda}(\bar{x}_d - DL)^2)^{1/2} .$$

Step 6. Use the corrected values of $\bar{X}$ and S in the procedure for constructing a tolerance interval (Section 5.3) or a confidence interval (Section 6.2.1).

REFERENCE

Cohen, A. C., Jr. 1959. "Simplified Estimators for the Normal Distribution When Samples are Singly Censored or Truncated." *Technometrics*. 1:217-237.

EXAMPLE

Table 8-3 contains data on sulfate concentrations. Three observations of the 24 were below the detection limit of 1,450 mg/L and are denoted by "< 1,450" in the table.

Step 1. Calculate the mean from the m = 21 values above detection

$$\bar{x}_d = 1,771.9$$

Step 2. Calculate the sample variance from the 21 quantified values

$$S_d^2 = 8,593.69$$

TABLE 8-3. EXAMPLE DATA FOR COHEN'S TEST

Sulfate concentration (mg/L)
1,850
1,760
< 1,450
1,710
1,575
1,475
1,780
1,790
1,780
< 1,450
1,790
1,800
< 1,450
1,800
1,840
1,820
1,860
1,780
1,760
1,800
1,900
1,770
1,790
1,780

DL = 1,450 mg/L

Note: A symbol "<" before a number indicates that the value is not detected. The number following is then the limit of detection.

Step 3. Determine

$$h = (24-21)/24 = 0.125$$

and

$$\gamma = 8593.69/(1771.9-1450)^2 = 0.083$$

Enter Table 7 of Appendix B at $h = 0.125$ and $\gamma = 0.083$ to determine the value of λ. Since the table does not contain these entries exactly, double linear interpolation was used to estimate $\lambda = 0.14986$.

REMARK

For the interested reader, the details of the double linear interpolation are provided.

The values from Table 7 between which the user needs to interpolate are:

γ	h = 0.10	h = 0.15
0.05	0.11431	0.17935
0.10	0.11804	0.18479

There are 0.025 units between 0.01 and 0.125 on the h-scale. There are 0.05 units between 0.10 and 0.15. Therefore, the value of interest (0.125) lies (0.025/0.05 * 100) = 50% of the distance along the interval between 0.10 and 0.15. To linearly interpolate between the tabulated values on the h axis, the range between the values must be calculated, the value that is 50% of the distance along the range must be computed and then that value must be added to the lower point on the tabulated values. The result is the interpolated value. The interpolated points on the h-scale for the current example are:

$0.17935 - 0.11431 = 0.06504$ $\qquad$ $0.06504 * 0.50 = 0.03252$
$0.11431 + 0.03252 = \underline{0.14683}$

$0.18479 - 0.11804 = 0.06675$ $\qquad$ $0.06675 * 0.50 = 0.033375$
$0.11804 + 0.033375 = \underline{0.151415}$

On the γ-axis there are 0.033 units between 0.05 and 0.083. There are 0.05 units between 0.05 and 0.10. The value of interest (0.083) lies (0.0330.05 * 100) = 66% of the distance along the interval between 0.05 and 0.10. The interpolated point on the γ-axis is:

$0.141415 - 0.14683 = 0.004585$ $\qquad$ $0.004585 * 0.66 = 0.0030261$
$0.14683 + 0.0030261 = \underline{0.14986}$

Thus, $\hat{\lambda} = 0.14986$.

Step 5. The corrected sample mean and standard deviation are then estimated as follows:

$$\bar{X} = 1{,}771.9 - 0.14986\ (1{,}771.9 - 1{,}450) = 1{,}723.66$$

$$S = [8{,}593.69 + 0.14986(1{,}771.9 - 1{,}450)^2]^{1/2} = 155.31$$

Step 6. These modified estimates of the mean, $\bar{X} = 1723.66$, and of the standard deviation, $S = 155.31$, would be used in the tolerance or confidence interval procedure. For example, if the sulfate concentrations represent background at a facility, the upper 95% tolerance limit becomes

$$1723.7 + (155.3)(2.309) = 2082.3 \text{ mg/L}$$

Observations from compliance wells in excess of 2,082 mg/L would give statistically significant evidence of contamination.

INTERPRETATION

Cohen's method provides maximum likelihood estimates of the mean and variance of a censored normal distribution. That is, of observations that follow a normal distribution except for those below a limit of detection, which are reported as "not detected." The modified estimates reflect the fact that the not detected observations are below the limit of detection, but not necessarily zero. The large sample properties of the modified estimates allow for them to be used with the normal theory procedures as a means of adjusting for not detected values in the data. Use of Cohen's method in more complicated calculations such as those required for analysis of variance procedures, requires special consideration from a professional statistician.

TABLE 7. VALUES OF THE PARAMETER $\hat{\lambda}$ FOR COHEN'S ESTIMATES ADJUSTING FOR NONDETECTED VALUES

h / τ	.01	.02	.03	.04	.05	.06	.07	.08	.09	.10	.15	.20	h / τ
.00	.010100	.020400	.030902	.041583	.052507	.063627	.074933	.086488	.098214	.110200	.173420	.242680	.00
.05	.010331	.021294	.032225	.043350	.054670	.066189	.077909	.089834	.101971	.114311	.179250	.250330	.05
.10	.010930	.022082	.033398	.044902	.056294	.068483	.080568	.092832	.105344	.118044	.184790	.257410	.10
.15	.011310	.022798	.034446	.046218	.058334	.070586	.083009	.093629	.106465	.121468	.189650	.264050	.15
.20	.011642	.023438	.035432	.047629	.059990	.072339	.085280	.098216	.111335	.124690	.194600	.270310	.20
.25	.011932	.024076	.036377	.048858	.061522	.074372	.087413	.100665	.114068	.127772	.199510	.276260	.25
.30	.012243	.024658	.037269	.050018	.062968	.076196	.089435	.102995	.116677	.130838	.203338	.281930	.30
.35	.012529	.025211	.038077	.051120	.064345	.077736	.091355	.105213	.119164	.133353	.207473	.287370	.35
.40	.012784	.025738	.038866	.052173	.065660	.079352	.093193	.107326	.121550	.135895	.211329	.292660	.40
.45	.013036	.026243	.039624	.053182	.066921	.080845	.094958	.109326	.123777	.138447	.215317	.297845	.45
.50	.013279	.026726	.040332	.054153	.068135	.082301	.096657	.111221	.125895	.140990	.218822	.302953	.50
.55	.013513	.027196	.041054	.055089	.069306	.083708	.098296	.113006	.127906	.143225	.222235	.307923	.55
.60	.013739	.027646	.041733	.055995	.070439	.085068	.099887	.114690	.129811	.145322	.225578	.312844	.60
.65	.013956	.028067	.042391	.056874	.071538	.086386	.101432	.116266	.131709	.147773	.227910	.316300	.65
.70	.014171	.028513	.043030	.057728	.072603	.087670	.102932	.117837	.133402	.149867	.230234	.320665	.70
.75	.014378	.028927	.043652	.058556	.073643	.088917	.104398	.120004	.135390	.151962	.232550	.324468	.75
.80	.014579	.029330	.044256	.059364	.074655	.090133	.105830	.121687	.137272	.154000	.234858	.327903	.80
.85	.014773	.029723	.044845	.060153	.075642	.091319	.107219	.123225	.138932	.155998	.237158	.331704	.85
.90	.014967	.030107	.045425	.060923	.076606	.092477	.108584	.124680	.140526	.157793	.244432	.337033	.90
.95	.015154	.030482	.045988	.061676	.077548	.093611	.109967	.126232	.142297	.159863	.247460	.340911	.95
1.00	.015338	.030850	.046540	.062413	.078471	.094720	.111118	.127780	.144463	.161700	.250022	.344711	1.00

h / τ	.25	.30	.35	.40	.45	.50	.55	.60	.65	.70	.80	.90	h / τ
.00	.31882	.4021	.4941	.5961	.7096	.8386	.9806	1.145	1.336	1.561	2.176	3.283	.00
.05	.32793	.4130	.5066	.6101	.7252	.8540	.9994	1.166	1.358	1.585	2.203	3.314	.05
.10	.33682	.4223	.5184	.6234	.7400	.8703	1.017	1.183	1.379	1.608	2.229	3.345	.10
.15	.34460	.4320	.5296	.6361	.7542	.8860	1.035	1.204	1.400	1.630	2.255	3.378	.15
.20	.35255	.4422	.5403	.6483	.7678	.9012	1.051	1.222	1.419	1.651	2.280	3.405	.20
.25	.35993	.4510	.5506	.6600	.7810	.9158	1.067	1.240	1.439	1.672	2.305	3.435	.25
.30	.36700	.4595	.5604	.6713	.7937	.9300	1.083	1.257	1.457	1.693	2.329	3.464	.30
.35	.37379	.4676	.5699	.6821	.8060	.9437	1.098	1.274	1.476	1.713	2.352	3.492	.35
.40	.38033	.4755	.5791	.6927	.8179	.9570	1.113	1.290	1.494	1.732	2.376	3.520	.40
.45	.38668	.4831	.5880	.7029	.8295	.9700	1.127	1.306	1.511	1.751	2.398	3.547	.45
.50	.39276	.4904	.5967	.7129	.8406	.9826	1.141	1.321	1.528	1.770	2.421	3.573	.50
.55	.39870	.4976	.6051	.7225	.8517	.9950	1.155	1.337	1.545	1.788	2.443	3.601	.55
.60	.40447	.5045	.6133	.7320	.8623	1.007	1.168	1.351	1.561	1.806	2.465	3.628	.60
.65	.41006	.5114	.6213	.7412	.8729	1.019	1.182	1.366	1.577	1.824	2.486	3.654	.65
.70	.41555	.5180	.6291	.7502	.8832	1.030	1.195	1.380	1.593	1.841	2.507	3.679	.70
.75	.42090	.5245	.6367	.7590	.8932	1.042	1.207	1.394	1.608	1.858	2.528	3.705	.75
.80	.42615	.5308	.6441	.7676	.9031	1.053	1.220	1.408	1.624	1.875	2.548	3.730	.80
.85	.43122	.5370	.6515	.7761	.9127	1.064	1.232	1.422	1.639	1.892	2.568	3.754	.85
.90	.43622	.5430	.6586	.7844	.9222	1.074	1.244	1.435	1.653	1.908	2.588	3.779	.90
.95	.44115	.5490	.6656	.7925	.9314	1.085	1.255	1.448	1.668	1.924	2.607	3.803	.95
1.00	.44582	.5548	.6724	.8003	.9406	1.095	1.267	1.461	1.682	1.940	2.626	3.827	1.00

For all values $0 \leq \tau \leq 1$, $\lambda(0,\tau) = 0$.

SOURCE: Cohen, A. C., Jr. 1961. "Tables for Maximum Likelihood Estimates: Singly Truncated and Singly Censored Samples." *Technometrics*.